AQUATIC EFFECTS TECHNOLOGY EVALUATION (AETE) PROGRAM

Assessing Aquatic Ecosystems Using Pore Waters and Sediment Chemistry

AETE Project 3.2.2a

Assessing Aquatic Ecosystems Using
Pore Waters and Sediment Chemistry

by

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Natural Resources Canada
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Contract No. NRCan 97-0083

Final Report

December 31, 1998

AQUATIC EFFECTS TECHNOLOGY EVALUATION PROGRAM

Notice to Readers

Assessing Aquatic Ecosystems Using Pore Waters and Sediment Chemistry

The Aquatic Effects Technology Evaluation (AETE) program was established to review appropriate technologies for assessing the impacts of mine effluents on the aquatic environment. AETE is a cooperative program between the Canadian mining industry, several federal government departments and a number of provincial governments; it is coordinated by the Canada Centre for Mineral and Energy Technology (CANMET). The program was designed to be of direct benefit to the industry, and to government. Through technical and field evaluations, it identified cost-effective technologies to meet environmental monitoring requirements. The program included three main areas: acute and sublethal toxicity testing, biological monitoring in receiving waters, and water and sediment monitoring.

The technical evaluations were conducted to document certain tools selected by AETE members, and to provide the rationale for doing a field evaluation of the tools or provide specific guidance on field application of a method. In some cases, the technical evaluations included a go/no go recommendation that AETE takes into consideration before a field evaluation of a given method is conducted.

The technical evaluations were published although they do not necessarily reflect the views of the participants in the AETE Program. The technical evaluations should be considered as working documents rather than comprehensive literature reviews. The purpose of the technical evaluations focused on specific monitoring tools. AETE committee members would like to stress that no one single tool can provide all the information required for a full understanding of environmental effects in the aquatic environment.

For more information on the monitoring techniques, the results from their field application and the final recommendations from the program, please consult the AETE Synthesis Report to be published in the spring of 1999.

Any comments concerning the content of this report should be directed to:

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PROGRAMME D'ÉVALUATION DES TECHNIQUES DE MESURE D'IMPACTS EN MILIEU AQUATIQUE

Avis aux lecteurs

Évaluation des écosystèmes aquatiques au moyen de l'eau de porosité et de la chimie sédimentaire

Le Programme d'évaluation des techniques de mesure d'impacts en milieu aquatique (ÉTIMA) visait à évaluer les différentes méthodes de surveillance des effets des effluents miniers sur les écosystèmes aquatiques. Il est le fruit d'une collaboration entre l'industrie minière du Canada, plusieurs ministères fédéraux et un certain nombre de ministères provinciaux. Sa coordination relève du Centre canadien de la technologie des minéraux et de l'énergie (CANMET). Le programme était conçu pour bénéficier directement aux entreprises minières ainsi qu'aux gouvernements. Par des évaluations techniques et des études de terrain, il a permis d'évaluer et de déterminer, dans une perspective coût-efficacité, les techniques qui permettent de respecter les exigences en matière de surveillance de l'environnement. Le programme comportait les trois grands volets suivants : évaluation de la toxicité aiguë et sublétale, surveillance des effets biologiques des effluents miniers en eaux réceptrices, et surveillance de la qualité de l'eau et des sédiments.

Les évaluations techniques ont été menées dans le but de documenter certains outils de surveillance sélectionnés par les membres d'ÉTIMA et de fournir une justification pour l'évaluation sur le terrain de ces outils ou de fournir des lignes directrices quant à leur application sur le terrain. Dans certains cas, les évaluations techniques pourraient inclure des recommandations relatives à la pertinence d'effectuer une évaluation de terrain que les membres d'ÉTIMA prennent en considération.

Les évaluations techniques sont publiées bien qu'elles ne reflètent pas nécessairement toujours l'opinion des membres d'ÉTIMA. Les évaluations techniques devraient être considérées comme des documents de travail plutôt que des revues de littérature complètes. Les évaluations techniques visent à documenter des outils particuliers de surveillance. Toutefois, les membres d'ÉTIMA tiennent à souligner que tout outil devrait être utilisé conjointement avec d'autres pour permettre d'obtenir l'information requise pour la compréhension intégrale des impacts environnementaux en milieu aquatique.

Pour des renseignements sur l'ensemble des outils de surveillance, les résultats de leur application sur le terrain et les recommandations finales du programme, veuillez consulter le Rapport de synthèse ÉTIMA qui sera publié au printemps 1999.

Les personnes intéressées à faire des commentaires concernant le contenu de ce rapport sont invitées à communiquer avec M^{me} Geneviève Béchard à l'adresse suivante :

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Executive Summary

Pore (or interstitial) water toxicity and sediment chemistry are important components of assessments which determine the bioavailability of contaminants in waterways receiving mining discharges. The methods and approaches used in pore water toxicity and sediment chemistry evaluations vary widely in their scope, application, sensitivity, accuracy and precision, resource requirements, scientific credibility, and effectiveness for mining applications. This technical evaluation provides an extensive review of the literature with subsequent recommendations based on consensus opinions of scientific peer-reviewed studies, technical reports, and experts from academia, industry, consulting, and government.

Pore water has been shown to be a major route of exposure for many benthic organisms. Contaminants in pore waters can be transported into overlying waters through diffusion, bioturbation, and resuspension processes. Contamination of the sediments and their surrounding pore waters may, therefore, adversely impact the aquatic ecosystem and interlinking food webs. The usefulness of pore water sampling for determining chemical contamination and/or toxicity will depend on the study objectives and nature of the sediments at the study site. Depositional sediments usually are the primary sediments of concern as they are generally the sites of highest contamination.

The literature on contaminated sediments reveals some trends and generalities, as follows: 1) There has been a tremendous increase in peer-reviewed publications and funded projects dealing with contaminated sediments in the past few years; 2) The focus on determining the bioavailable fractions of contaminants is clearly established as superior to "total" chemical concentrations for assessing ecosystem harm; 3) The "weight-of-evidence" approach utilising a combination of physicochemical, habitat, indigenous biota, and toxicity characterisations is now widely accepted as the superior approach to contaminant assessments, reducing uncertainty of single "tool" approaches; 4) Detection of sediment contamination is much more sensitive with improved analytical methods and sublethal indicators of toxicity and stress; 5) Sediments are complex and variable in nature; 6) Sampling and laboratory testing of sediments can significantly alter contaminant bioavailability; 7) Contaminated sediments are degrading numerous aquatic ecosystems; and 8) Pore water toxicity testing is used to a lesser extent than whole sediment toxicity testing.

Predicting what fraction of the total metal concentration is bioavailable is a challenge, since metals complex to varying degrees with so many different entities and their toxicity rapidily changes with speciation and complexation. However, it is apparent that bioavailability can be determined and sound conclusions derived if proper methods and quality assurance protocols are used. This technical evaluation resulted in the following conclusions: 1) Pore water toxicity testing provides a useful supplement to whole sediment testing; 2) Pore water metal concentrations may be the best sediment chemistry indicator of bioavailability; 3) Metal concentrations which exceed water quality criteria should be considered harmful; 4) Pore water toxicity testing must be done using carefully controlled collection, extraction, and testing conditions to ensure reliable results; 5) Pore water toxicity testing should only be conducted if adequate QA/QC guidelines are followed; 6) *In situ* peeper collection of pore waters is the most accurate method, reducing sampling artifacts for chemical analysis and toxicity tests which can be conducted with small sample volumes; 7) *In situ* sample collection and/or testing is preferable to laboratory extraction and/or testing; 8) Efforts must be made to reduce sampling related artifacts, such as oxidation and mixing of vertical gradients; 9) Toxicity testing should commence as soon as possible following extraction; 10) Centrifugation (10,000 x g, 30 min.,

4°C) without filtration is the preferred pore water extraction method if *in situ* collection methods are not feasible; 11) Few laboratories have experience with pore water toxicity testing; however, qualified laboratories do exist in Canada; 12) Total metal concentrations in sediments are most reliable in situations where gross contamination exists; 13) Easily extractable fractions may be useful on a site specific basis, but are still considered to be in the realm of research; 14) The AVS/SEM approach shows promise with some metals in anaerobic sediments, such as Cd and Ni; 15) Dissolved organic C is likely a primary control factor for Cu availability; and 16) An integrated assessment approach is most accurate, combining toxicity testing, biological community characterization, habitat characterization, and physicochemical characterization in a tiered testing approach.

Given the need to adopt a uniform national approach to environmental assessments, it would be useful to conduct a field demonstration project at geologically diverse mining sites to better evaluate utility of pore water toxicity testing. This evaluation program should include field validation of the popular sediment quality guidelines for routine application in mining monitoring situations. Following this demonstration project, appropriate guidelines should be developed for regulatory application of pore water toxicity testing.

Sommaire

La toxicité de l'eau interstitielle (ou eau de porosité) et la chimie des sédiments occupent une place importante dans les évaluations visant à déterminer la biodisponibilité des contaminants dans les cours d'eau recevant des effluents miniers. Les méthodes et les approches utilisées dans le cadre de ces évaluations varient considérablement quant à leur portée, leur application, leur sensibilité, leur exactitude et leur précision, leurs exigences en ce qui a trait aux ressources, leur crédibilité scientifique et leur applicabilité au secteur minier. Les responsables de la présente évaluation technique ont effectué un examen approfondi de la documentation pertinente et formulé une série de recommandations fondées sur les conclusions d'études révisées par des pairs, des rapports techniques et l'opinion de spécialistes provenant d'universités, de l'industrie, d'entreprises d'experts-conseils et du gouvernement.

Il a été démontré que l'eau interstitielle est une importante voie d'exposition aux contaminants pour de nombreux organismes benthiques. Les contaminants présents dans l'eau interstitielle peuvent se propager aux couches d'eau sus-jacentes par diffusion, bioturbation et remise en suspension. La contamination des sédiments et des couches d'eau interstitielle avoisinantes peut dès lors avoir des conséquences néfastes pour les écosystèmes aquatiques et les chaînes trophiques qui leur sont associées. L'utilité relative des échantillonnages d'eau interstitielle réalisés à des fins d'évaluation de la contamination chimique et de la toxicité dépend des objectifs de la recherche et de la nature des sédiments dans la zone étudiée. Parmi les sédiments, ce sont les dépôts d'alluvions qui soulèvent les préoccupations les plus importantes en raison de leur niveau de contamination généralement très élevé.

L'examen de la documentation consacrée à la contamination des sédiments a permis de dégager les tendances et généralités suivantes : 1) le nombre de publications révisées par les pairs et de projets financés consacrés aux sédiments contaminés s'est accru considérablement au cours des quelques dernières années; 2) la supériorité de l'approche privilégiant le dosage des fractions de contaminants biodisponibles sur celle prévoyant le dosage des concentrations totales, en vue d'évaluer les dommages causés aux écosystèmes, est clairement établie ; 3) l'approche fondée sur le poids de la preuve utilisant une combinaison de variables liées aux propriétés physico-chimiques, à l'habitat, aux espèces indigènes et à la toxicité est maintenant largement reconnue comme la meilleure approche pour évaluer les problèmes causés par les contaminants en raison du fait qu'elle permet notamment de réduire l'incertitude des approches prévoyant le recours à des outils uniques; 4) l'amélioration des méthodes d'analyse et la mise au point d'indicateurs sublétaux de la toxicité et du stress ont permis d'accroître considérablement la sensibilité des méthodes de détection de la contamination des sédiments; 5) la nature des sédiments est à la fois complexe et variable; 6) l'échantillonnage et les analyses des sédiments en laboratoire peuvent modifier considérablement la biodisponibilité des contaminants; 7) la contamination des sédiments entraîne la dégradation de nombreux écosystèmes aquatiques; 8) la toxicité de l'eau interstitielle est moins fréquemment évaluée que celle des sédiments totaux.

Il est difficile de prévoir quelle fraction de la concentration totale de métaux est biodisponible, car les métaux peuvent former divers complexes renfermant un très grand nombre d'entités différentes, et leur toxicité varie rapidement en fonction du type de composés chimiques et des complexes. Il est cependant possible de déterminer la biodisponibilité des métaux totaux et de formuler des conclusions solides en utilisant les méthodes et les protocoles d'assurance de la qualité appropriés. La présente évaluation permet de tirer les conclusions suivantes : 1) l'évaluation de la toxicité de l'eau interstitielle constitue un complément utile à

l'analyse des sédiments totaux; 2) les concentrations de métaux dans l'eau interstitielle pourraient s'avérer les meilleurs indicateurs de la biodisponibilité liés à la chimie des sédiments; 3) les concentrations de métaux qui dépassent les normes de qualité de l'eau doivent être considérées comme dangereuses; 4) pour faire en sorte que les résultats des essais de toxicité de l'eau interstitielle soient fiables, il faut contrôler minutieusement toutes les étapes du prélèvement, de l'extraction et des essais; 5) l'évaluation de la toxicité de l'eau interstitielle doit être effectuée seulement si les lignes directrices appropriées relatives à l'AQ et au CQ sont respectées; 6) la collecte "peeper" *in situ* d'échantillons d'eau interstitielle est la méthode la plus fiable, car elle permet de réduire les artefacts liés à l'échantillonnage pour les analyses chimiques et les essais de toxicité qui peuvent être effectués à partir d'échantillons de faible volume; 7) le prélèvement et(ou) l'analyse des échantillons *in situ* est(sont) préférable(s) à l'extraction et à l'analyse en laboratoire; 8) toutes les précautions voulues doivent être prises pour réduire les artefacts liés à l'échantillonnage (p. ex. oxydation, mélange des gradients verticaux); 9) les essais de toxicité doivent être entrepris le plus rapidement possible après l'extraction; 10) la centrifugation (10 000 x g, 30 min., 4 °C) en l'absence de filtration est considérée comme la meilleure méthode d'extraction de l'eau interstitielle lorsque les méthodes de collecte *in situ* s'avèrent impraticables; 11) s'il est vrai qu'un très faible nombre de laboratoires possèdent l'expérience nécessaire pour évaluer la toxicité de l'eau interstitielle, il existe quelques laboratoires qualifiés au Canada; 12) la fiabilité des concentrations de métaux totaux dans les sédiments est optimale en cas de contamination sévère; 13) les fractions facilement extractibles peuvent fournir des renseignements utiles sur certains sites, mais leur utilisation est encore confinée au domaine de la recherche; 14) la méthode d'extraction simultanée des métaux / sulfite acide volatil semble efficace pour le dosage de certains métaux dans les sédiments anaérobiques (p. ex. Cd et Ni); 15) le carbone organique dissous joue vraisemblablement un rôle déterminant dans la disponibilité du Cu; 16) le recours à une approche d'évaluation intégrée prévoyant la réalisation d'essais de toxicité et l'examen des caractéristiques des communautés biologiques et de l'habitat et des propriétés physico-chimiques permet d'obtenir des résultats d'une grande précision.

Étant donné la nécessité d'adopter une approche nationale uniforme pour les évaluations environnementales, il convient d'entreprendre un projet de démonstration sur le terrain dans des sites miniers présentant des caractéristiques géologiques différentes afin de mieux évaluer l'utilité des essais de toxicité de l'eau interstitielle. Ce programme d'évaluation devrait comporter une étape de validation sur le terrain des lignes directrices sur la protection et la gestion des sédiments aquatiques en vue d'une application systématique à la surveillance des effets de l'activité minière sur les écosystèmes aquatiques. Une fois ce projet de démonstration mené à bien, il faudrait élaborer des lignes directrices en vue de l'application réglementaire des essais de toxicité de l'eau interstitielle.

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1. Introduction

This technical evaluation focuses on the use of pore (interstitial) water toxicity and sediment chemistry in assessments of metal bioavailability in waterways receiving mining discharges. Both of these media have been used often in assessments of contaminated sediments. However, the methods and approaches used vary widely in their scope, application, sensitivity, accuracy and precision, resource requirements, scientific credibility, and effectiveness for mining applications. The evaluation provides an extensive review of the literature (Table 1) with subsequent recommendations based on consensus opinions of scientific peer-reviewed studies, technical reports, and experts from academia, industry, consulting, and government.

Pore water is defined as the water occupying space between sediment or soil particles, often isolated to provide either a matrix for toxicity testing or to provide an indication of the concentration and partitioning of contaminants within the sediment matrix. The United States Environmental Protection Agency (U.S. EPA) sediment quality criteria are based on the assumption that the primary toxicity of a chemical is correlated to the pore water concentration, suggesting that it is a major route of exposure (Di Toro *et al.* 1991). However, this route of exposure does not include uptake from ingestion of contaminated sediment particles. In addition, contaminants in pore waters can be transported into overlying waters through diffusion, bioturbation, and resuspension processes (Van Rees *et al.* 1991). The usefulness of pore water sampling for determining chemical contamination and/or toxicity will depend on the study objectives and nature of the sediments at the study site. Sediments which are either very coarse-grained (such as gravel or cobble) or hard, compacted clays will likely not have pore waters which are significantly contaminated. Therefore, sampling of pore waters should be restricted to sediments ranging from sandy to non-compacted clays. Pore waters from depositional zones containing finer-grained sediments (e.g., clays) are usually the most contaminated because of the large surface area and binding capacity of clays and their associated components (*e.g.*, organic matter, iron and manganese oxyhydroxides).

There have been several comprehensive reviews and comprehensive guidance documents in recent times dealing with assessments of contaminated sediments and metal bioavailability (Burton 1991, Campbell *et al.* 1988; Mudroch and MacKnight 1991, ASTM 1994, Ingersoll *et al.* 1997, Environment Canada 1994, Chapman *et al.* 1997, Campbell and Tessier 1994, Tessier and Turner 1995, Hill *et al.* 1994). Many of the issues reviewed in these documents are relevant to the subjects of this Technical Evaluation (TE). As one surveys the literature on contaminated sediments there are some conspicuous trends and generalities, as follows: 1) There has been a tremendous increase in peer-reviewed publications and funded projects dealing with contaminated sediments in the past few years; 2) The focus on determining the bioavailable fractions of contaminants is clearly established as superior to "total" chemical concentrations for assessing ecosystem harm; 3) The "weight-of-evidence" approach utilising a combination of physicochemical, habitat, indigenous biota, and toxicity characterisations is now widely accepted as the superior approach to contaminant assessments, reducing uncertainty of single "tool" approaches; 4) Detection of sediment contamination is much more sensitive with improved analytical methods and sublethal indicators of toxicity and stress; 5) Sediments are complex and variable in nature; 6) Sampling and laboratory testing of sediments can significantly alter contaminant bioavailability; 7) Contaminated sediments are degrading numerous aquatic ecosystems; and 8) Pore water toxicity testing is used to a lesser extent than whole sediment toxicity testing. These trends and generalities are of particular importance to the objective of this project. Many of these issues will be addressed in more detail in the following sections.

Table 1. Principal Information Sources for the Technical Evaluation.

Computer Databases:

- Biological Abstracts
- Scientific Citations
- Toxline
- Medline
- OhioLink (all Ohio university libraries)

Other Libraries (Periodicals, Books, Technical Reports):

- Wright State University
- Library of G. Allen Burton

Natural Resources Canada:

- Canadian Technical Reports (regulatory and mining)

Surveys:*

- Environment Canada
- U.S. Geological Survey
- U. S. Environmental Protection Agency
- British Columbia Ministry of Environment
- EVS Consultants, Ltd.
- PTI, Inc.
- BEAK Ltd.
- Phillips Analytical, Ltd.
- ENSR Corp.
- Kennecott Mines
- ChemRisk Division of McClaren Hart Corp.
- Commonwealth Scientific and Industrial Research Organization of Australia
- National Institute of Water and Atmospheric Research of New Zealand
- Noranda Technology Centre
- Water Research Centre, Ltd. of England
- Coimbra University, Portugal
- National Hydrobiological Institute, Italy
- Stirling University, Scotland
- Colorado State University
- CETESB, Sao Paulo, Brazil

* Voice survey dealt with knowledge of relevant studies/literature, opinions on relevant issues, and cost effectiveness. Multiple individuals were contacted within some organizations. Many institutions also provided publications.

Acknowledgment: I particularly wish to thank Madona Skaff (CANMET), Peter Chapman (EVS) , Graeme Batley (CSIR Australia), and Bill Stubblefield (ENSR) for their useful contributions. AETE Technical Committee members provided valuable review comments on draft reports.

Any effects of metals on living organisms result from biological uptake of the fraction of total metal present in the test media (*e.g.*, sediment, water, soil, and food). While "total" metal concentrations are significantly correlated with biological effects in many studies, this is likely a function of the study design such as comparing grossly contaminated sites with lightly contaminated sites. So, the correlation is simply a covarying phenomenon and crudely related to the smaller bioavailable fraction. It is well established that in some environmental samples, none of the total metal may be bioavailable. However, total metal concentrations in sediments may be orders of magnitude higher than in overlying waters. So very small changes in metal exchange from sediment to pore or overlying waters may exert significant biological effects (Luoma 1989). Predicting what fraction of the total metal concentration is bioavailable is a challenge, since metals complex to varying degrees with so many different entities and their toxicity rapidily changes with speciation and complexation. This TE will review the methods used to predict metal bioavailability in sediments and pore waters using toxicity, biomarkers, bioaccumulation, metal ion calculations, and selective extractions. In each case, the strengths and weaknesses of the approaches are considered.

2. Assessments Using Sediment Pore Water

2.1. Overview of Methods

A variety of chemical and biological methods exist for documenting increases or decreases in metal bioavailability, including: physicochemical analyses, modeling, biotic characterization, toxicity testing, and biomarkers in both laboratory and *in situ* settings. Biomarkers have not been used to any appreciable extent with pore waters, but have potential applications in assessments of sublethal exposures to contaminants.

2.2. Pore Water Chemistry and Linkage with Metal Sources

2.2.1. Metal Partitioning in Sediments

Metals tend to easily and quickly complex with organic and inorganic compounds. Their degree of association or binding affinity varies markedly, however, and is difficult to predict in natural systems. Metal cations frequently implicated with contamination include Cd, Cr, Cu, Pb, Ni, and Zn. Arsenic and Se are usually present as anionic forms and are metalloids whose environmental fate is dominated by different sorption properties. As discussed in Section 3, metals are bound to a variety of sediment fractions of Fe and Mn oxides and organic materials and range from easily extractable (and bioavailable) to resistent residual mineral phases (*e.g.*, Tessier *et al.* 1979; Jenne 1968, 1977; Luoma and Davis 1983; Davies-Colley *et al.* 1984; Campbell *et al.* 1988; Campbell and Tessier 1994). Freshly discharged or dissolved metals which enter aquatic ecosystems can be present as free ions, but tend to occur as ferro- or manganese oxyhydroxide, carbonate, or sulfide complexes (*e.g.*, Burton 1991, Chapman *et al.* 1997).

There have been many studies in recent years describing the important role of acid volatile sulfide (AVS) in binding metals in anoxic sediments (*e.g.*, Ankley *et al.* 1996, DiToro *et* *al.* 1992). The AVS is a procedurally defined fraction (1 N HCl extraction) containing the relatively labile Fe and Mn monosulfides as the dominant component (Morse *et al.* 1987). Other trace metals such as Cd, Cu, Pb, Ni, and Zn will displace Fe and Mn from sulfide. Their stronger binding with sulfide makes them unavailable for uptake by aquatic organisms (Di Toro *et al.* 1992). AVS can be formed microbially, as organic matter is oxidized in anaerobic environments where sulfate is the electron acceptor. Several studies have shown that in sulfide-dominated sediment systems, metal acute toxicity only occurs when the individual or sum molar concentration of simultaneously extracted metal (SEM) exceeds the AVS concentration; thereby allowing free metal ion activity in pore waters (Di Toro *et al.* 1990, 1992; Ankley *et al.* 1991; Carlson *et al.* 1991; Hare *et al.* 1994; Leonard *et al.* 1995; Pesch *et al.* 1995). However, other binding phases with various sulfides and polysulfides, oxyhdroxides, inorganic and organic C are important in controlling bioavailability and may dominate in some sediments, as discussed below.

The importance of iron and manganese oxyhydroxides (FeOOH and MnOOH) in complexation of trace metals has been known for over two decades. It was first shown in dredging studies that oxyhydroxides (*e.g.*, $Fe(OH)_3$) quickly scavenged (minutes to hours) metals which were released during dredging into the overlying waters (see Burton 1991). However, only a small fraction of the metal may be released during these resuspension events (Förstner 1995; Zhuang *et al.* 1994). The importance of the resuspension event on metal release will be a function of several factors, such as length of oxidation period, occurrence of fresh iron or manganese oxyhydroxides, and the SEM to AVS ratio. Tessier *et al.* (1996) and others (*e.g.*, Dzombak and Morel 1990; Smith and Jenne 1991) showed surface complexation of trace metals by iron and manganese oxides and oxyhydroxides. The effect of metal remobilization from sediments into overlying oxidized waters can result in acute toxicity (Carvalho *et al.* 1998). Predicted binding constants closely agreed with laboratory derived surface complexation values. These phenomena are only dominant in aerobic environments, thus are of significance in surficial sediments (*e.g.*, 0 to 2 mm depth) and during resuspension and diffusion events. Nonetheless, due to the occurrence of Fe and manganese oxyhydroxides in virtually all freshwater ecosystems and since macrofauna primarily reside in aerobic environments, the role of oxyhroxides in controlling metal bioavailability is of tremendous importance. Complexation with metals will likely be occurring in close proximity ($\leq$ 1 mm) to anoxic zones where AVS may be the dominant binding phase.

Another very important binding phase in many freshwater aquatic systems is organic C (both dissolved and particulate). Organic C binds metals in aerobic or anaerobic sediments (Fu *et al.* 1992; Mahony *et al.* 1996; Tessier *et al.* 1993; Wang *et al.* 1997). The form of organic C, its complexation and resulting bioavailability varies widely and much work remains to be done to describe its role. Ion-binding (Marinsky and Ephraim 1986), surface complexation (Davis 1984; Tessier *et al.* 1993) and binding with humics (Mahony *et al.* 1996; Tipping and Hurley 1992) have been shown to be important in determining metal fate. Binding has been described using the Humic Ion Binding Model V (Hare and Tessier 1996; Tipping and Hurley 1992) and using the Langmuir adsorption model (Mahony *et al.* 1996). Complexation with soluble ligands (e.g., humics) can increase metal mobilization, thereby increasing bioavailability. There are exceptions to the free metal ion model, with other metal forms being toxic. Many scientists have shown higher metal concentrations in pore waters than predicted based on partitioning (Emerson *et al.* 1983; Huerta-Diaz *et al.* 1997). Binding to organic C can reduce the bioavailability (toxicity) of metals (Nebeker *et al.* 1986). It is well documented that the speciation of Cu solutions is dominated by complexation with natural organic matter (Teasdale *et al.* 1996), with inorganic species typically < 1%. However, in oxic sediments binding substrates for Cu may be Fe and Mn oxyhydroxides also with high correlations noted with Fe oxides (Teasdale *et al.* 1996). Partitioning studies between interstitial and sediment-bound Cu in Canadian Shield lakes and UK rivers (with suspended solids) have found distribution coefficients of 0.83 to 1.9 L/g (Martin and Whitfield 1981). In oxic sediments, particulate Cu typically have log Kd values of 1 to 2 in the pH range of 6-8. However, in anoxic sediments, the insolubility of CuS results in immobilization of Cu (Teasdale *et al.* 1996).

Inorganics, such as carbonates, are well known in aquatic toxicology and water quality criteria studies as important complexors of metals. High concentrations of carbonates in some mine overburden may prevent acidification arising from sulfate-reducing bacteria and thus buffer pore water Cu concentrations (Teasdale *et al.* 1996). Other species such as hydroxyls, fluorides, chlorides, sulfides, polysulfides, sulfates, thiols (such as cysteine, glutathione, methanethiol) and phosphates complex metals in aerobic and/or anoxic aquatic environments (Newman and Jagoe 1994; Huerta-Diaz *et al.* 1997; MacCrehan and Shea 1995), however, their role and formation is not well defined at present.

Another very important factor in metal binding is the surface characteristics of solids and competition from other ions (Benjamin and Leckie 1981; Laxen 1983; Schindler 1981). Sediment fractions that have a high cation exchange capacity or are easily reduced are typically the most bioavailable (Khalid *et al.* 1981; Luoma 1983, 1989; Gunn *et al.* 1989).

The partitioning process is obviously a complicated one, based on all these potential complexation agents and processes, many of which are occurring simultaneously or in close proximity to each other with organisms being exposed to multiple forms of a metal. This complexity heightens the importance of toxicity testing to verify effects that may occur from the system as a whole (described below). Assumptions of binding constants, sediment-pore water equilibrium, and free ion activity can always be challenged, yet there are an increasing number of studies which are clearly documenting the usefulness of these approaches in defining metal fate and effects.

Undoubtedly, the most dynamic and biological important zone of the sediment environment is the surficial zone (top 2 cm). In depositional sediments, the top 1 to 2 mm are often the only layer which is oxic (Carlton and Klug 1990). The sharply changing redox environment, microbial, meiofaunal, and macrofaunal populations, diagenic processes, and bioturbation which occur in the top few cm of depositional sediments creates microenvironments on the sub-mm scale which vary in oxidation, complexation capacity, and contaminant bioavailability. Describing this system is a challenge. The tools exist, however, to describe the bioavailability of toxic metals in sediments.

Near the sediment-water interface, where the redox gradient quickly changes, metal sulfide complexes (*e.g.*, AVS/SEM) may become oxidized due to oxygen diffusion, bioturbation, advection or resuspension processes (*e.g.*, Burton 1991; Gonzalez 1996; Millero *et al.* 1987; Peterson *et al.* 1996; Zhuang *et al.* 1994). When AVS oxidation occurs, free metal ions are released which may cause toxicity. A monodisperse particle surface oxidation model based on particle morphology, pH, ionic strength and dissolved oxygen describes the oxidation of FeS which is similar to AVS (Di Toro *et al.* 1996a). Each metal has a different binding affinity with sulfide which will affect its dissolution and displacement rate. For example, CdS oxidizes much slower than FeS and synthesized CdS oxidation rates do not reflect pore water concentrations (Di Toro *et al.* 1996b).

The near surface zone of oxidation has been shown to vary in depth and magnitude temporally on a diurnal to seasonal basis. The subsequent dissolution of sulfide complexes will vary with the metal and site specific conditions and cannot be readily predicted without site data.

Spatial and temporal variations are due to a host of factors such as: benthic periphyton photosynthesis, settling of phytoplankton, other organic inputs, bioturbation, water currents, temperature, microbial reduction of sulfate, and other physical disruptions (Besser *et al.* 1996; Carlton and Klug 1990; Gagnon *et al.* 1996; Hansen *et al.* 1996a; Howard and Evans 1993; Leonard *et al.* 1993; Liber *et al.* 1996; Matisoff *et al.* 1995; Peterson *et al.* 1996; Tessier *et al.* 1989). Cu flux out of sediments is higher in freshly deposited or disturbed sediment (Apte *et al.* 1997). Aeration of laboratory or field sediments can decrease AVS and reduce metal binding capacity (Zhuang *et al.* 1994; Hare *et al.* 1994; Leonard *et al.* 1995).

2.2.2. Prediction of Metal Concentrations in Sediments and Pore Waters

The prediction of biological exposure and effects from metal contaminated sediments is possible using a variety of methods. Normalization of total or extractable fractions of metals using AVS (*e.g.*, Ankley *et al.* 1996ab; Di Toro *et al.* 1990, 1992), organic C (Ankley *et al.* 1996ab; Campbell and Tessier 1994; Mahony *et al.* 1996; Tessier and Campbell 1987), and Fe hydroxide (Campbell and Tessier 1994; McDonald 1993; Tessier and Campbell 1987) can improve correlations with biological effects. When AVS is low, then sediment metal normalization may be controlled by particulate organic carbon (POC) and/or Fe oxyhydroxides. In these studies Fe was extracted with $NH_2OH.HCl$ (Tessier *et al.* 1984) or HCl (Bryan 1985) and normalized with *in situ* collected diagenetic Fe (Tessier *et al.* 1993) and POC (Tessier *et al.* 1993). These normalizations even surpassed total dissolved Cd (Tessier *et al.* 1993).

The effects resulting from organisms residing in or on contaminated sediments can be due to particulate ingestion, dermal sorption, or ingestion of pore and overlying waters. The exposure route will vary with the species life history and feeding characteristics and the site conditions. For example, benthic organisms residing in the sediments (*e.g.*, tube dwellers) or on the sediments (molluscs and crustaceans) can be significantly affected by metals in overlying waters due to their bioirrigation and bioturbation activities (Chapman *et al.* 1997; Deaver and Rodgers 1996; O'Donnel *et al.* 1985; Hare and Tessier 1996; Tessier *et al.* 1993). Bascombe *et al.* (1990) showed that amphipods exposed to one pulse concentration of Zn in overlying water died weeks later after the Zn migrated from outer chitin layers to internal organs. This shows that surface sorption phenomena are important and may include subsequent transport mechanisms. In addition, organisms may receive most of their metal exposure from food (Munger and Hare 1997; Stephenson and Turner 1993) or from sediment fractions such as organic C and Fe oxyhydroxides (Tessier *et al.* 1993). So, in conclusion, prediction of bioavailable metal concentrations requires consideration of sources from sediment, pore water, food, and overlying water.

In the mid-1980's the U.S. EPA began promoting the use of acid volatile sulfides (AVS) as a normalization factor for sediments contaminated with metals (*e.g.*, DiToro *et al.* 1991; Ankley *et al.* 1996ab). Since that time there has been extensive research investigating the role of AVS in binding of cationic metals such as Cd, Cu, and Ni (*e.g.,* Ankley *et al.* 1996ab). In summary, these studies have found the following:

1. When the Simultaneously Extracted Metal (SEM) fraction exceeds the AVS fraction (molar ratio) (SEM:AVS>1), then free metal may be present in the pore water at levels adequate to cause acute toxicity,
2. When SEM:AVS is < 1, then metal toxicity likely does not exist in the sediments (which assumes that pore waters are the major route of exposure),
3. Some metals, such as Cu, may not be controlled by AVS; rather, they are controlled by organic C complexation,
4. AVS varies spatially and seasonally in lake sediments (Howard and Evans 1993),

5. Clear associations with other metals, such as Cr, Pb, As, and Se have not been established with AVS, and
6. Bioaccumulation has not been assessed thoroughly in relation to SEM:AVS.

Recently, Cooper and Morse (1998) showed that the methods used to determine SEM:AVS ratios could underestimate the potential bioavailability of several metals of importance in anoxic sediments. This is because the HCl extraction does not effectively extract some S forms which complex Cu, Hg, and Ni, and surface area also affects the apparent solubility in HCl.

A number of models exist which can predict the distribution and speciation of metals in aquatic systems, including sediments and pore waters. Previously mentioned was the Humic Ion Binding Model V which is included with other submodels in WHAM (Version 1.0). This model allows incorporation of biotic receptor sites of metals and non-biotic ligands to be considered in calculations of metal availability (Tipping 1994). Other useful models include: FITEQL (Version 3.2, Herbelin and Westall 1996), HYDRAQL (Papelis *et al.* 1988), MINEQL+ (Version 3.01, Schecher and McAvoy 1994), and MINTEQA2 (Version 3.11, Allison *et al.* 1991). These models, however, have not been shown to be useful to date, for determining metal bioavailability and require further field validation. Specific shortcomings of these thermodynamically-based approaches are: assume solid-water equilibrium; constants based on 25°C which is warmer than many sediments; constants often based on low ionic strength water (unlike many pore waters); formation and sorption constants of many key metal complexes (*e.g.*, sulfide containing, Fe and manganese containing, organic matter) not known; and crystalline forms and solubility of various metal sulfides are not well defined (Chapman *et al.* 1997).

Thermodynamic calculations on oxic pore waters and sediments show trace metals tend to be undersaturated. Therefore, solubility equilibrium with solids is unlikely and the sorption of metals to surfaces is a dominant mechanism in the fate of trace metals (Tessier and Campbell 1987; Schindler 1975). An adsorption-based model to predict trace metal partitioning in sediments has been suggested (Oakley *et al.* 1981). Adsorption models require information on equilibrium constants, number of binding sites, and binding intensities of each component (*e.g.*, metal oxyhydroxides, organics, carbonates) which is difficult to obtain in natural sediments at this time (Luoma and Davis 1983; Tessier and Campbell 1987). However, overall equilibrium constants have been calculated and compared between lab and field successfully and showed the influence of pH on adsorption of various metals (Tessier and Campbell 1987). It is interesting to note that in freshly prepared artificial sediments, surface area and porosity of fresh and aged Fe oxyhydroxides varied dramatically and altered metal ion sorption (Benjamin and Leckie 1981; Crosby *et al.* 1983; Tessier and Campbell 1987). Additional information on partitioning in various sediment fractions is discussed in Section 3.0.

The Free Ion Activity Model (FIAM) suggests that free metal ions (Me^{2+} or $Me(H_2O_x^{2+}$) are the most bioavailable form of metal. Campbell (1995) and Chapman *et al.* (1997) provide excellent reviews of the FIAM. The model is based on the assumption that metal interacts with organisms via a surface complexation on the plasma membrane, whereby the response is proportional to the free ion activity after surface complexation sites are saturated. FIAM appears to work well in situations where there is low dissolved organic C and several field lidation studies have documented its usefulness (Campbell 1995; Hare and Tessier 1996; Tessier *et al.* 1993). A number of sediment studies have also shown a relationship between metal bioavailability in sediments and pore water free metal ion concentration (Ankley *et al.* 1993; Berry *et al.* 1996; De Witt *et al.* 1996; Di Toro *et al.* 1990, 1992; Kemp and Swartz 1986; Sibley *et al.* 1996; Swartz *et al.* 1985). In some situations, however, the model does not correctly predict bioavailable metal concentrations which are toxic as other metal complexations are occurring which are not considered (*e.g.*, with hydroxyl complexes (Cowan *et al.* 1986; Fisher 1986), organometallic species, oxyanions, humics (Stackhouse and Benson 1989) and non-chemical variables (Erickson *et al.* 1996; Chapman *et al.* 1997)). The gills of fish have been shown to have receptor sites which are competitive ligands for trace metal binding, competing with natural dissolved organic matter. There is a strong relationship between mortality and gill receptor site saturation (MacRae 1994). This biotic site (gill) complexation model suggests that it is unwise to generalize that one metal species is more available than another since the gill causes chemical re-equilibration to occur (Chapman *et al.* 1997).

Chapman *et al.* (1997) suggest that a simple relationship between biological effects and normalized sediment concentrations, or free metal ion activity in pore water or overlying water can predict metal bioavailability in sediments These relationships assume the metal sources (pore water, overlying water, and food) are in equilibrium and additive, and the metal concentration in food is proportional to the free metal ion in the digestive tract. Perhaps the biggest drawback for the free ion model approach is the lack of analytical methods to verify free ion concentrations. This may be overcome by normalizing dissolved metal concentrations with water-only toxicity measurements (Berry *et al.* 1996; Hansen *et al.* 1996ab) and pore water toxicity units (Ankley *et al.* 1996b). Pore water toxicity units may be used for deriving sediment quality criteria for metals (Ankley *et al.* 1996b). This approach shows potential but has been little tested, using only total metal concentrations and acute toxicity effects. Further studies measuring bioaccumulation and chronic effects are needed.

Despite the apparent complexity of predicting metal bioavailability in sediments (*e.g.*, knowing the route of exposure and the form and concentration of the toxic species), it is apparent from the success of many studies that metal toxicity can be predicted in sediments.

2.2.3. Toxicity Identification Evaluations

Toxicity Identification Evaluations (TIE) were originally developed by the U.S. EPA for identifying which contaminants in wastewater effluents were the primary contributors to toxicity (U.S. EPA 1991abc). The TIE approach fractionates and manipulates a sample, removing or reducing different chemical classes (*e.g.*, metals, nonpolar organics) and alters sample toxicity by altering chemical availability (*e.g.*, pH, aeration, filtration). The resulting subsamples are then used in acute to short-term chronic toxicity tests. These manipulations allow the investigator to determine which contaminant(s) are most likely to be causing harm in the test sample. More detailed evaluations (Phase 2 or 3) provide additional chemical testing of the fractions to better identify the problem contaminants.

Whole Sediments. There are active research efforts on-going in several laboratories focused on development of TIE methods for whole sediments. However, there are no accepted or peer-reviewed methods which are available at this time.

Pore Waters. In the U.S. EPA standard pore water TIE test, metals are identified by adding EDTA (ethylenediamine tetraacetate), a chelating agent, to the pore water and then measuring any resulting changes in acute toxicity to *Ceriodaphnia dubia* or *Pimephales promelas* (U.S. EPA 1991abc). Approximately 1.2 liters of pore water are required to test each organism in the miniaturized exposure design. Modifications to the method include short term chronic toxicity exposures, where pore waters are renewed in the test beakers weekly. The problems with pore water quantity and possible alteration of metal bioavailability from storage and manipulation of the sediments are accentuated in the chronic exposures. More recently, chelex as been tried as a metal chelating agent (Davison and Zhang 1994) and may be an alternative to EDTA in the TIE.

Few studies have been conducted which utilize TIE procedures for evaluating which are the primary toxicants in pore waters (Ankley *et al.* 1991; Schubauer-Berigan and Ankley 1991, and Wenholz and Crunkilton 1995). These studies have shown toxicity due to metals, ammonia, nonpolar organics and solids-associated contaminants. A difficulty with these TIE procedures is that the quantity of pore water needed requires substantial sediment collection and processing. As with the effluent TIE methods, toxicity is frequently lost in the fractionation process or non-detectable with acute methods. Recently, Burton and Rowland (1995) modified the TIE Phase 1 methods for pore waters to focus on metals, ammonia, non-polar organics, and photoactivated polycyclic aromatic hydrocarbons (PAHs). Their testing has found ammonia and PAHs are frequently the cause of toxicity in depositional sediments from urban watersheds.

2.2.4. Source Identification

Sources of sediment contamination can be identified using pore water data. Physical, chemical, biological, or toxicity testing of sediments does not directly identify sources, but when an adequate test design is utilized which considers all watershed inputs and monitors parameters unique to the source, then accurate identifications are possible. Specific examples of source identification are presented below in Sections 2.3 and 3.0.

2.3. Linking Pore Water Chemistry with Biological Effects

2.3.1. Bioavailability Issues: Overview

There is an abundance of literature documenting the important role of pore water as a primary route of exposure for sediment dwelling organisms (*e.g.*, Burton 1991). The preponderance of data indicating pore water's significance led to the development of the U.S. EPA sediment quality guidelines for nonpolar organics and AVS using the equilibrium partitioning approach (*e.g.*, Di Toro *et al.* 1991). In summary, many studies have shown that acute toxicity of benthic organisms is strongly correlated with pore water chemistry when concentrations exceed water column-based lethal thresholds. These thresholds were based on a very large water quality criteria database (water only) which appears to be applicable to pore water thresholds. At the same time, however, there is a large literature base that shows both benthic and non-benthic species are also exposed to sediment contaminants via ingestion and dermal sorption (*e.g.*, Burton 1991). These additional exposure routes may play a greater role in studies of chronic toxicity and bioaccumulation, and the importance of each exposure route is obviously dependent on the species life history and feeding behavior.

A variety of factors in sediments affect the bioavailability of metals in pore waters (Campbell *et al.* 1988; Campbell and Tessier 1994). The extensive work of the U.S. EPA and others in field validation of the equilibrium partitioning (EqP) approach has shown that the assumptions of EqP theory do hold up in many cases where acute toxicity and high levels of contamination exist. That is, TOC or AVS normalization of nonpolar or divalent metal concentrations showed threshold exceedances resulted in degraded benthic communities. This field validation however, has only be done with a handful of chemicals, such as Cd, Ni, DDT, endrin, dieldrin, and polycyclic aromatic hydrocarbons (PAHs). Cu availability may be dominated by AVS, but is also strongly influenced by organic matter (Ankley *et al.* 1996a). In addition, carbonates may play a significant role, as they do in overlying waters. Iron and manganese oxyhydroxides complex rapidly with dissolved metals as documented in early studies focused on dredging impacts (Gambrell *et al.* 1976; Salomons 1985; Oscarson *et al.* 1981). Surface binding affinities are very important for some species of metals and vary in strength between metals and vary with surface types, as discussed earlier.

Sediment-bound methyl and inorganic mercury availability to the marine mussel *Mytilus edulis* was studied by labelling Fe and manganese oxides, montmorillonite clay, and silica with and without organic coatings. Fulvic acid coatings enhanced sorption of both inorganic and methylated Hg onto all particles, with low assimilation efficiencies for inorganic Hg (II) and >30% for methylated Hg. Unlike Cd, Co, and Ag, there was little Hg desportion from sediments at pH 5. Results showed Hg (particularly $CH_3Hg(II)$ is readily available from sediments by suspension feeders (Gagnon and Fisher 1997).

Perhaps the most complicating factor associated with using pore waters to assess bioavailability is the fact that contaminant partitioning and speciation may be altered through the collection and testing process. There are numerous papers in the limnological and oceanographical literature addressing the influence of sampling methods on pore water chemistry (*e.g.*, reviews in Burton 1991, ASTM 1994). What is less clear, however, is whether these alterations result in significant changes in toxicity of pore waters (bioavailability). For labile species, such as ammonia, the results of sampling can be very significant (Sarda and Burton 1995). The results of sediment manipulation via grab or core sampling with subsequent centrifugation may be an increased concentration of the toxicant in the pore water, providing a possible worst case scenario (Sarda and Burton 1995). If sediment agitation introduces oxygen, then AVS may be reduced resulting in higher levels of bioavailable metals in the pore water. A competing reaction exists when oxidation occurs, however, by metal complexation with Fe and manganese oxyhydroxides thereby reducing bioavailability.

Care should be taken to reduce the oxidation and mixing process when sampling and preparing sediments for toxicity testing or pore water testing. The use of *in situ* collection devices such as peepers are advantageous since they reduce sampling related artifacts, but create some logistical challenges in deep water or fast flowing environments.

The potentially negative aspects of the oxidation process continue on through the toxicity test exposure, as samples must be aerated for the test organisms. Benthic organisms living in fast flowing, steep gradient, stream environments are usually associated with sand, gravel, and cobble substrates, where pore waters are oxidized. Sampling related artifacts are less likely with metal chemistry in these environments due to the lack of dynamic redox gradients and reducing microenvironments. In slower waters, where depositional zones exist, sediments are more silty and clayey in nature and pore waters are typically anoxic below the top 1 to 2 mm of sediment. These are the sediments where sampling is likely to reveal higher concentrations of contaminants and are therefore subject to sampling artifacts. Even though these sediments are anoxic, the benthic macroinvertebrate population lives primarily in an oxic microenvironment. This is accomplished by their pumping of overlying waters into their burrows, or simple physical agitation (bioturbation) of the sediment from crawling and burrowing during their feeding. Bioturbation is primarily restricted to the upper 6 cms of sediment. Strong advective pore water replacement down to a 5 cm sediment depth was shown due to pressure gradients from mussel shells. These provide a fast, conveyor-belt-type link between sediment layers as deep as 15 cm and the water column in sandy sediments (Huettel and Gust 1992). Kikuchi and Kurihara (1977) found the presence of a freshwater tubificid oligochaete, *Branchiura sowerbyi,* kept the activity of Fe^{2+} high in the upper 1 cm of sediment, increased the flux of Fe^{2+} into overlying water, enhanced ammonia concentrations in sediment, decreased the number of aerobic bacteria, and increased the number of sulfate-reducing bacteria throughout the sediment column. This same oligochaete burrows to 20 cm. An enhanced diffusion model best described their transport of solutes from sediments into overlying waters (Wang and Matisoff (1997).

There is a wealth of literature (*e.g.*, review by Campbell *et al.* 1988; Peterson *et al.* 1996; Matisoff and Robbins 1987; Matisoff *et al.* 1985) documenting the significant and widespread alterations which bioturbation can have on sediments, as follows: sediment compaction;

distribution of organic C and nitrogen; mass transport of gases; nitrification and denitrification; sulfate reduction; ammonia turnover; ratios of CO_2 and carbonates; and redox and pH profiles. Whether or not the oxic microenvironments surrounding the benthic macroinvertebrates significantly alter metal bioavailability from the surrounding anoxic environment, only sub-mm away, is unknown at this time. Increased rates of bioturbation increase the rate of internal manganese cycling in sediments (between oxidizing and reducing zones) more than they do the rate of cycling across the sediment surface (Sundby and Silverberg 1985). Simpson *et al.* (1998) suggest that FeS and MnS phases may buffer effects of bioirrigation and that trace metal sulfide phases may remain predominantly unoxidized for some time. However, any trace metals occluded in or co-precipitated with FeS phases may be particularly prone to oxidative release. Bioturbation is not restricted to benthic macroinvertebrates, but includes bottom-feeding fish. The koi carp was shown to remobilize Cd from sediments into overlying waters (Wall *et al.* 1996). Carlton and Klug (1990) showed that sediments which are anoxic become oxidized from benthic algae photosynthesis and exhibit a classic diurnal flux of oxygen which can increase the oxygen content markedly down several mm during the day. So there is definitely a potential for bioavailability changes over small distances (0 to 6 mm) due to natural biological activity. These changes do not appear to alter the acute toxicity of sediments, as evidenced by previously discussed field validations. They may, however, affect chronic toxicity of pore waters.

2.3.2. Biological Community Characterization: Overview

This topic is the focus of another Technical Evaluation, so is limited in scope. No studies were found on biological communities which only focused on pore waters. There is obvious application, however, of many aquatic ecosystem and whole sediment studies of metal contamination whereby pore water contamination was an integral route of exposure to biological communities. The most directly applicable are assessments of benthic macroinvertebrate communities and indigenous microbial community enzyme activities (Burton and Stemmer 1987; Mills and Cowell 1977). These studies have documented several population, community, functional level, and enzymatic response endpoints as sensitive indicators of significant metal contamination in sediments. Another issue not being covered in this TE, but of profound importance in the assessment of biological effects are the biological processes affecting bioavailability. Processes which affect metal bioavailability and uptake include: digestion or extracellular secretions, physiological transport across membranes, transformation and storage within the organism, seasonal physiological changes (*e.g.*, reproduction), age, adaptation, intra- and inter-species differences in bioaccumulation, and feeding strategy (Luoma 1989; Hare 1992; Hare and Shooner 1995; Hare *et al.* 1989, 1991, 1998). If there is not a general understanding of these issues by the investigator or for the assessment methods (*e.g.*, single species bioassay) being used, then resulting conclusions of metal bioavailability will be tenuous.

2.3.3. Toxicity and Biomarker Testing

There are many peer-reviewed studies dealing with pore water toxicity testing. However, there are fewer pore water studies than studies dealing with whole sediments. The U.S. EPA has chosen not to develop standard methods with pore waters as whole sediment testing is more realistic. A limited amount of testing has been conducted with pore waters at mining sites.

The advantages of toxicity testing with pore waters as opposed to whole sediments are as follows:

- Easy to observe test organisms
- Greater variety of test organisms and assay types can be used
- Test organisms in direct contact (100%) with dissolved contaminants (readily bioavailable contaminant phase) and tends to be worst

case response, as compared to whole sediment or elutriate responses

- Can be used in sediment TIE approach

Disadvantages of pore water toxicity testing also exist, such as:

- Large quantity of sediment may be required to produce adequate volume (Note: Sarda and Burton (1995) obtained large quantities of pore water with *in situ* sampling of peepers. Modifications to other toxicity test methods substantially reduced volume requirements. (See p. 34 for additional information)
- Perhaps less realistic for organisms which are primarily sediment ingesters
- Few standard methods exist
- Long term exposures stressful to benthic organisms due to lack of sediment substrate

There are also other important considerations for the use of pore waters in routine monitoring programs. There is some degree of additional labour required for extracting pore water. In addition, faulty sample processing may introduce artifacts which may alter bioavailability (toxicity). Finally, pore water quality tends to change quickly with storage, so testing must be conducted within hours to days.

A wide range of freshwater and marine organisms have been tested in pore waters (Burton 1991). Unfortunately, few standardized pore water toxicity tests exist and those in existence are not for traditional freshwater benthic invertebrate surrogates. Environment Canada (1992ab) has two standard methods using pore water, which are for Echinoids (Sea Urchins and Sand Dollars) and luminescent bacteria (*Photobacterium phosphoreum/Vibrio fisherii).*

Ammonia is frequently present in sediments and may confound determinations of sediment toxicity. A new method for marine and estuarine pore water testing using the marine algae, *Ulva fasciata*, has been demonstrated (Hooten and Carr 1998). This algae is unaffected by high ammonia concentrations and therefore is useful in TIE studies where bioassays using ammonia sensitive bioassays (*e.g.,* sea urchin fertilization and embryological development) are used simultaneously. Whiteman *et al.* (1996) found good correspondence between LC50 values of water-only tests and spiked sediment tests for both *Lumbriculus variegatus* and *Chironomus tentans*. This verified the technical basis for defining ammonia bioavailability in sediment based on pore water concentrations.

A bacterial based assay has been proposed for heavy metal toxicity testing. The FluoroMetPLATE™ bioassay is based on the activity of *B*-galactosidase from a mutant of *Escherichia coli* and uses a fluorogenic substrate, 4-methylumbelliiferyl *B*-D-galactoside, as an enzyme substrate (Jung *et al.* 1996). The liquid assay was found to be specific for metals, more sensitive than Microtox®, and similar to *Ceriodaphnia dubia* (48 hr acute assay) with the exception of Pb. This simplistic assay has potential applications to pore water toxicity testing.

The Microtox® assay was modified for testing with solid samples whereby the bacteria *Photobacterium phosphoreum*, now known as *Vibrio fisherii*, contacts solids during the assay exposure (Ankley *et al.* 1989; Carlson-Ekvall and Morrison 1992; Chen and Morrison 1994). Toxicity due to solids associated metals has been shown (Carlson-Ekvall and Morrison 1992). Problems with using NaCl as an osmotic diluent have been studied, with suggested replacements (Carlson-Ekvall and Morrison 1995).

Two other microbial based bioassays which have been used in sediment extract testing include the ATP-TOX and Toxi-Chromotest asays (Brouwer and Murphy 1995). They were shown to be sensitive (as was the Microtox® assay) to the presence of reduced sulfur species in anoxic sediments.

Biomarkers are defined here as subcellular response measures of a biochemical, genetic, physiological, immunological, histological, or pathological nature. A large amount of research is being directed towards the use of biomarkers in ecotoxicological assessments. This includes studies of various cytochrome P450 enzymes (*e.g.*, EROD), metallothioneins, stress proteins, endocrine mimics and disruptors, and DNA fingerprinting. Many of these biomarkers have been found to be very sensitive indicators of exposure to contaminants; however, the ecological significance and specificity of the responses are, as yet, difficult to determine (Hugget *et al.* 1992; Benson & Di Guilio 1992; Decaprio 1997). A variety of biomarkers have been used in assessments of metal contamination, including metallothioneins, thiobarbituric acid reactive species (oxidative stress), glycogen, lipid, blood chemistry, and macrophage (Hamoutene *et al.* 1996; Pedersen *et al.* 1997; Meinelt *et al.* 1997; Benson and Di Giulio 1992). None of these have been directed towards pore waters specifically.

Metallothioneins are proteins induced by the presence of some metals and have particular promise as a biomarker. These proteins bind metals and appear to have a role in metal homeostasis and perhaps in the detoxification of trace, non-essential, metals such as Cd. They have been shown to be useful in contaminant assessments near metal smelter industries (Pedersen *et al.* 1997; Couillard *et al.* 1993) showing relationships with metals in contaminanted sediments. Variations in metallothionein in a freshwater bivalve were not related to dissolved or extractable metal concentrations, but to free Cd concentration at the sediment water interface as estimated from sediment-water sorptive equilibria (Couillard *et al.* 1993; Campbell and Tessier 1994). The analytical method for determining metallothioneins is relatively complex and not conducted on a routine basis.

Exposure to metals can also be assessed in some species for some metals, using a tissue residue (bioaccumulation) approach. As with biomarkers, bioaccumulation studies have not focused on pore water contamination, but rather whole sediments. The presence of metals in tissues is often a more sensitive measure of exposure than toxicity measures - which may or may not detect effects or exposure. As with toxicity testing, the presence of the metal often does not indicate the source of the metal. In a properly designed study however, the source, exposure period and gradient of contamination can be characterized. Long term bioaccumulation studies of pore water in laboratories are not feasible; however, *in situ* peeper exposures have potential use in coarse-grained sediments; but have yet to be done. Most use of bioaccumulation testing will involve whole sediments and may be conducted via predictions using sediment bioaccumulation models. These models have primarily focused on nonpolar organics and assume equilibrium and steady state conditions between the organism and the environment or kinetic approaches that describe bioaccumulation as the net effect of rate processes (Lee 1992; Chapman 1997). Several studies have shown the usefulness of bioaccumulation in assessing the risks of metal contaminated sediments to the aquatic ecosystem (Ankley *et al.* 1996a; Chapman 1996; Munger and Hare 1997; Woodward *et al.* 1993; Luoma 1989). Simple correlations between total metals in sediments and tissue concentrations in benthic organisms are usually weak (*e.g.*, Luoma 1989). However, stronger relationships are possible: by normalization of sediments with key components (*e.g.*, AVS, Fe oxide, organic C, particle size), by using geochemically similar environments where feeding is more selective and limits exposure to one dominant form of metal, or where large gradients in metal concentrations exist (Luoma 1989).

An issue which some suggest is a major drawback in the use of toxicity testing of pore waters is whether the subsequent oxidation of the sample during the bioassay exposure is relevant, as it may have no relationship to *in situ* conditions (MDA 1997). However, this opinioin is flawed. It is true that most pore waters from depositional areas (where clays and silts predominate) are anoxic. Bioassay test organisms cannot survive without oxygen, thus the pore water sample must be aerated to some degree to meet test performance criteria. While some bacterial populations are anaerobes and require anoxic conditions, all meiofaunal and macrofaunal organisms are aerobes and require oxygen to varying degrees. Many of these organisms of concern are benthic and inhabit near-surface sediments where they create aerobic microenvironments through their feeding, burrowing, and filtration behaviors. While they may contact anoxic pore waters, their presence initiates the oxidation process. Unfortunately, research has been limited in defining relationships between contaminants, redox gradients and benthic organisms in their micro-environments. In addition, there is a limited understanding of organism responses to contaminants which diffuse from sediments and pore waters or from resuspended sediments. Each of these phenomena initiate the oxidation process. If the primary issue of concern is metal bioavailability/effects to the macrofaunal communities, then oxidation of pore waters during test exposures is appropriate and reflects real world exposures. Since the bioavailability of chemicals change over time, then pore water oxidation should be minimized and limited until bioassay initiation. If pore waters were oxidized and stored for extended periods, then ensuing sorption and partitioning processes continue and the uncertainty of their resemblance to *in situ* conditions increases. In summary, pore water toxicity testing in the laboratory is a reasonable simulation of natural conditions, if samples are collected and processed properly and the bioassay exposures are realistic.

The issue of oxidation and toxicity testing of extracted pore waters is irrelevant if toxicity testing is conducted *in situ*. *In situ* toxicity testing of pore waters via peepers is preferable, but cannot be conducted when pore waters are anoxic (Fisher 1991). Its use is limited to coarse-grained, aerobic sediments which exist in some marine and high power freshwater stream environments.

2.3.3.1. Sediment and Pore Water Dilutions

It is useful in some studies to obtain precise effect-level information to better characterize gradients of effects or threshold levels. This can be done by diluting either spiked (dosed) sediments or by diluting sediments or pore waters.

A "clean" noncontaminated sediment should be used as the "diluent". This sediment should optimally have characteristics similar to the test sediment, such as organic matter/C concentration, particle size distribution, salinity, and not contain elevated levels of the toxicants. In order to obtain concentration-effects information in solid phase toxicity testing, diluting a test sediment with a clean non-contaminated sediment has been suggested as an approach (Burton 1991; Chapman 1987). Dilutions of test sediments have been performed with reference or control sediments (DeWitt *et al.* 1989; Giesy *et al.* 1990; Pastorok and Becker 1990; Swartz *et al.* 1989; Nelson *et al.* 1993; Tay *et al.* 1992). Dilutions with test sediment have generally led to reductions in the toxicity of the diluted test material relative to the original (undiluted) test sediment. However, when sand was used as a diluent, the toxicity decreased and then subsequently increased for some sediments (Nelson *et al.* 1993) although the sand alone was not toxic compared to controls. The mechanism for this effect is not known. Where described, the dilutions were generally mixed to visual homogeneity and the only report of a definitive storage time after mixing was for 10 d (Giesy *et al.* 1990; Tay *et al.* 1992) and the temperature for storing diluted sediments was 4°C (Giesy *et al.* 1990). There is no consensus on the amount of time necessary for re-equilibration of sediments prior to toxicity testing. The actual amount of dilution can be estimated by determining the fraction of fine material and the organic C content in the reference sediment, test sediment and diluted material (Nelson *et al.* 1993). Little information exists on the most appropriate method for diluting test sediments to obtain graded contaminant concentrations. The same can be said for what is known about the role of sediment composition, equilibrium time, and alteration of chemistry during mixing on the exposure to the test sediment contaminants in the diluted material.

No standard guidance exists for dilution of pore waters. This, however, is more straightforward than dilution of whole sediments. Pore waters should be diluted with the same considerations as dilutions of surface waters, effluents, elutriates and leachates. These considerations include using dilution waters of appropriate hardness, alkalinity, pH, and oxygen content. If the pore water is to be diluted immediately prior to toxicity testing, then the presence of dissolved oxygen is less of an issue. However, if the pore water is to be diluted and stored for more than a few hours, then preserving the original D.O. level is important to reduce the oxidation process.

Some critical issues to consider when diluting sediments are:

1) The proper equilibration time and spiking method to use in studies where artificial sediments are spiked with contaminants is dependent on the study objectives, chemical type, sediment type, target species behavior, and exposure system. Unfortunately, few studies have investigated these issues in a critical manner. Short-term equilibration will better mimic recent chemical events and long-term equilibration will better mimic historical chemical events.

2) Dilutions of whole sediments should be conducted with caution. Diluting with a reference sediment of similar characteristics is recommended; however, dynamic and uneven shifts in equilibrium among the serial dilutions will likely result in non-linear responses with inadequate equilibration times. If pore waters are to be isolated, they should be extracted prior to the dilution process and then diluted directly.

3) For reference toxicant testing, sediment dilutions are more straightforward and should be conducted with the appropriate test substrate, *e.g.*, artificial sediments (described above). Spiking with metals such as Cd only requires mixing periods of 1 to 4 hours while mixing of nonpolar organics may require several hours of mixing following by an equilibration period of 2

to 4 weeks. It is advisable to document that equilibration conditions exist (via chemical analysis), particularly when there will be extended exposure periods in subsequent toxicity testing.

2.4. Pore Water Sample Collection and Manipulation Issues

2.4.1. Collection Methods

Isolation of sediment pore water can be accomplished by a wide variety of methods, which can be grouped as laboratory- or field- (*in situ*) based. The common laboratory-based methods can be categorized as: 1) centrifugation, 2) pressurization, or 3) suction. Field-based methods include suction and "peepers" (for reviews, see Adams *et al.* 1986; ASTM 1994; Burton 1992; Environment Canada 1994; Mudroch and MacKnight 1991). Peepers are small diffusional chambers with membrane or mesh walls, filled with site water, gels/substrates, or nonpolar solvents, which are buried in sediments and surrounding pore water then equilibrates within the chamber. Chambers are typically retrieved from 2 to 20 days after deployment.

When relatively large volumes of water are required (such as 20 mL or greater), grab and core sampling with subsequent centrifugation (*e.g.*, Giesy *et al.* 1988; Landrum *et al.* 1987; Burgess *et al.* 1993; Ankley *et al.* 1990, 1991; Schubauer-Berigan and Ankley 1991; Edmunds and Bath 1976; Engler *et al.* 1977; Jahnke 1988; Kalil and Goldhaker 1973; Reeburgh 1967) and sediment squeezing (Carr *et al.* 1989; Long *et al.* 1990) methods are typically used. Other methods such as suction (Watson and Frickers 1990; Whitman 1989; Pittinger *et al.* 1988; Knezovich and Harrison 1987) and *in situ* samplers may not easily produce sufficient volumes for most required analyses. Recently, larger sized peepers (500 mL volume) have been used recently for collecting chemistry samples and for exposing test organisms *in situ* (Burton 1992; Sarda and Burton 1995).

Most sediment collection and processing methods have been shown to alter pore water chemistry (*e.g.*, Schults *et al.* 1992; Bufflap and Allen 1995ab; Sarda and Burton 1995; Janssen *et al.* 1995) and, therefore, potentially alter contaminant bioavailability and toxicity. Some important pore water constituents, (*e.g.*, dissolved organic C, dimethylsulfide, ammonia, major cations, and trace metals) can be significantly altered by the collection method (*e.g.*, Lyons *et al.* 1979; Howes *et al.* 1985; Sayles *et al.* 1973; Bischoff *et al.* 1970); Martin and McCorkle 1993; Carignan *et al.* 1994; Bufflap and Allen 1995ab; Sarda and Burton 1995). Increased sample handling associated with methods such as grab or core sampling and centrifugation, squeezing, or suction, may cause significant increases in key constituents, such as ammonia, sulfide, and DOC concentrations as compared to those collected via *in situ* "peepers" or core-port suction. Other constituents, such as salinity, dissolved inorganic C, sulfide, and sulfate, might not be affected by collection, providing oxidation is prevented. If sediments are anoxic, as most depositional sediments are, all steps involved in sample processing should be conducted in inert atmospheres or by limited contact with the atmosphere to prevent oxidation (and subsequent sorption/precipitation) of reduced species (Lyons *et al.* 1979; Howes *et al.* 1985; Bray *et al.* 1973). When anoxic sediments are exposed to air, volatile sulfides will be lost which may increase the availability of sulfide-bound metals (Zhuang *et al.* 1994). In addition, Fe and manganese oxyhydroxides are quickly formed which readily complex with trace metals, thus altering metals-related toxicity (*e.g.*, Bray *et al.* 1973; Troup *et al.* 1974; Burton 1991). Sampling via grab or core in combination with storage (oxic vs anoxic) were the most important factors affecting toxicity of extracted pore waters. The highest toxicity generally occurred with grab samples stored under oxic conditions. Higher toxicity was also observed in centrifuged vs squeezed samples. Extraction atmosphere, temperature or filtration were of minor importance (Janssen *et al.* 1995). Other studies, however have shown filtration to significantly reduce toxicity (Stemmer *et al.* 1990).

The need for maintaining anoxic conditions during processing is not necessary when the study objectives are only concerned with exposures to oxic sediments, or if target contaminants are unaffected by oxidation in short-term toxicity or bioaccumulation testing. For example, in the United States studies of dredged material toxicity do not consider ammonia as a contaminant and oxidation is actually promoted to remove ammonia from overlying waters of the toxicity test beakers. In depositional sediments where small particle sizes predominate, the oxic layer is usually only the upper 1 to 2 mm of sediment (Carlton and Wetzel 1985). These macroinvertebrates require oxygen to live (albeit low levels for some organisms), but their oxygenated micro-environment allows them to exist in anoxic sediments. This reality supports the use of standardized toxicity tests, whereby overlying waters must be aerated in order to measure chemically related toxicity. The process of sediment collection will introduce oxidation without careful precautions being taken, however, a limited degree of oxidation is acceptable since macrofauna require oxygen. Benthic invertebrates, however, create micro-gradients of oxidized sediments within anoxic sediments in their immediate surrounding through bioturbation and circulation of overlying waters into their burrows. Oxidation also occurs when sediment-bound chemicals are released to overlying waters via resuspension, advection, and diffusion processes.

Immediate collection of pore water is recommended since chemical changes might occur even when sediments are stored for short periods (*e.g.*, 24 h) at *in situ* temperatures (Hulbert and Brindle 1975; Watson *et al.* 1985; Sarda and Burton 1995). The optimal collection method will depend upon the purpose of sample (*e.g.*, acidification for metal analysis and not toxicity testing), characteristics of the sediment, and the contaminants of concern. Sediments which are highly contaminated with strongly non-polar organics (such as PCBs) are not likely to change in toxicity.

Isolation of Pore Water by Centrifugation

The conditions for isolation of pore waters by centrifugation have varied considerably. For toxicity testing, pore waters have been isolated over a range of centrifugal forces and temperature ranges (Giesy *et al.* 1988; Landrum *et al.* 1987; Burgess *et al.* 1993; Ankley *et al.* 1990, 1991; Schubauer-Berigan and Ankley 1991; Edmunds and Bath 1976; Engler *et al.* 1977; Ankley and Schubauer-Berigan 1994; Schults *et al.* 1992) with centrifuge bottles of various compositions. When centrifugation followed by filtration has been compared with *in situ* dialysis, higher speed centrifugation followed by filtration with 0.2 µm membrane filters has produced results that were more similar for metals and organic C (Jenne and Zachara 1987; Carignan *et al.* 1985). Centrifugation at low speeds or use of a larger pore size filtration membrane (*e.g.*, 45 µm mesh) will result in retention of dissolved contaminants, colloidal materials, and aquatic bacteria in the pore water sample (Jenne and Zachara 1987). High speed centrifugation (*e.g.*, 10,000 x g) is necessary to remove colloids and dispersible clays (Adams 1991; Chin and Gschwend 1991; Brownawell and Farrington 1986; Ankley and Schubauer-Berigan 1994). Typically, toxicity is reduced with high speed centrifugation or filtration due to the removal of particle-associated contaminants (Sasson-Brickson and Burton 1991; Ankley and Schubauer-Berigan 1994; Schults *et al.* 1992; Bufflap and Allen 1995a). While the duration of the centrifugation has been variable, 30 minutes is relatively common. The temperature for the centrifugation should reflect the ambient temperature of collection to ensure that the equilibrium between particles and pore water is not shifted.

Filtration through glass fiber or polycarbonate membranes may cause the loss of some dissolved metals and organics (Word *et al.* 1987; Schults *et al.* 1992). If filtration is employed, a nonfiltered sample should also be tested for toxicity and contaminant concentrations. The effects of centrifugation speed, filtration, and oxic conditions on some chemical concentrations in pore waters have been well documented (*e.g.*, Adams 1991; Klinkhammer 1980; Simon *et al.* 1985; Ankley and Schubauer-Berigan 1994; Schults *et al.* 1992; Bufflap and Allen 1995b; Bray *et al.* 1973). It is recommended that, for routine toxicity testing of pore waters, sediments should be centrifuged at 10,000 x g for a 30 min period at 4°C (ASTM 1994, Environment Canada 1994).

It is difficult to collect pore water from sediments that are predominately coarse sand. A modified centrifuge bottle has been developed with an internal filter that can recover 75% of the pore water as compared to 25 to 30% from squeezing (Saager *et al.* 1990).

All containers have been shown to adsorb various organic contaminants (Schults *et al.* 1992). Polytetrafluoroethylene (PTF), *e.g.*, Teflon, glass and stainless steel have all been shown to adsorb metals and organic compounds, acting as ion exchangers. However, sediments have many more binding sites than the container walls, and likely decrease the significance of container-associated loss in short term exposures. PTF bottles will collapse at 3000 g but have been used successfully up to 2500 g when filled to 80% of capacity (Burgess *et al.* 1993). Isolation of pore water in this case should be at the temperature of collection, at a slower speed of 2500 g for 30 min duration. This material will contain colloidal material as well as dissolved compounds. At low centrifugation speeds, without filtration, removal of the colloids may not be possible. The influence of dissolved and colloidal organic C may be estimated by measuring the organic C content. If small volumes of water are required for testing, higher speed centrifugation can be performed with glass tubes (up to 10,000 g) (Word *et al.* 1987). If metal related toxicity is not a concern, then high speed centrifugation in stainless steel centrifuge tubes is an option. When working with samples contaminated with organics, efforts should be made to reduce sample exposure to light to reduce photo-related degradation or alteration of any potentially toxic compounds. This can be accomplished by using amber bottles and yellow lights.

Isolation of Pore Water by Pressurization

Isolation of pore water by squeezing has been performed with a variety of procedures (Carr *et al.* 1989; Adams 1991; Boulegue *et al.* 1982; Jahnke 1988; Kalil and Goldhaker 1973; Reeburgh 1967; Long *et al.* 1990). In all cases, the pore water is passed through a filter that is a part of the apparatus. Filters have different sorptive capacities for different compounds. Numerous studies have shown filters reduce toxicity and contaminant concentrations by retaining contaminant associated particles and also by contaminant sorption onto the filter matrix (Schults *et al.* 1992; Bray *et al.* 1973; Troup *et al.* 1974; Sasson-Brickson and Burton 1991). The characteristics of filters and the filtering apparatus should be carefully considered. Squeezing has been shown to produce a number of artifacts due to shifts in equilibrium from pressure, temperature, and gradient changes (*e.g.*, Kalil and Goldhaker 1973; Sayles *et al.* 1973; Bischoff *et al.* 1970; Bollinger *et al.* 1992; Kriukov and Manheim 1982; Froelich *et al.* 1979; Schults *et al.* 1992; Troup *et al.* 1974). A reduction in electrolyte concentration in the pore water occurred when squeezing was conducted. It is, therefore, recommended that moderate pressures be used with electrolyte (conductivity) monitoring during extraction (Kriukov and Manheim 1982). Significant alterations to pore water composition occurred when squeezing was conducted at temperatures different from ambient (*e.g.*, Sayles *et al.* 1973; Bischoff *et al.* 1970). Other sources of alteration of pore water when using the squeezing method are: contamination from overlying water, internal mixing of pore water during extrusion, and solid-solution reactions as pore water is expressed through the overlying sediment. As pore waters are displaced into upper sediment zones, they come in contact with solids they are not in equilibrium with. This inter-mixing causes solid-solution reactions to occur. The chemistry of the sample may be altered due to the fast kinetics (minutes to hours) of these reactions, as observed with ammonia and trace metals (Rosenfeld 1979; Santschi *et al.* 1984). Bollinger *et al.* (1992) found elevated levels of several ions and dissolved organic C in squeezed samples as compared to samples collected by peepers. The magnitude of the artifact will depend on the element, sediment characteristics and redox potential. It is unlikely that reactive species gradients can be established via squeezing of sediment cores (Bender *et al.* 1987).

Isolation of Pore Water by Vacuum Filtration

Small volume isolation of pore water, generally for chemical analysis, can also be performed by vacuum filtration (Jenne and Zachara 1987; Knezovich and Harrison 1987; Winger and Lassier 1991), gas pressurization (Reeburgh 1967) or displacement after removing the sediment from the aquatic environment (Adams 1991). When preparing sediments for pore water isolation of metals, care must be taken to maintain the anoxic conditions of deeper sediments by performing the procedures under an inert atmosphere (Adams 1991). Suction using an aquarium air stone recovered up to 1,500 mL from 4 L of sediment suctioned in an anoxic environment (Santschi *et al.* 1984). Another suction method, using a hand vacuum attached to an aquarium stone was an effective method of collecting pore water (Winger and Lassier 1991; Sarda and Burton 1995). The air stone is attached to a 50 mL syringe via plastic tubing. The stone is inserted in the sediment to the desired depth and then suction applied. Clogging of the air stone is a problem in some sediments; however it is effective in most tested. The collection system can be purged of oxygen prior to leaving the laboratory. Ammonia concentrations in water obtained by this system were similar to those collected with *in situ* peepers (Sarda and Burton 1995). Problems common to suction methods are loss of equilibrium between the pore water and the solids, filter clogging, and oxidation (Brinkman *et al.* 1982). However, *in situ* suction or suction via core ports has been shown to accurately define small gradients of some sediment-associated compounds, including ammonia, the concentrations of which can vary by an order of magnitude over a 1 cm depth interval (Simon *et* *al.* 1985). However, these small-scale suction methods may not provide an adequate volume for conducting some traditional toxicity test procedures.

Isolation of Pore Water by In Situ Techniques

There are many studies which have demonstrated the usefulness of *in situ* collection methods (*e.g.*, Apte *et al.* 1997; Barnes 1973; Belzile *et al.* 1989; Bottomley and Bayly 1984; Buddensiek *et al.* 1990; Howes *et al.* 1985; Jahnke 1988; Mayer 1976; Murray and Grundmanis 1980; Sayles *et al.* 1973; Davison *et al.* 1991; Sarda and Burton 1995). Reviews of methods are also presented in ASTM (1994), Environment Canada (1994), Burton (1992), and Adams (1991). These methods of pore water collection are superior to more traditional methods in that they are less likely to alter the chemistry of the sample. The principal methods of pore water collection through the use of peepers (*e.g.*, Adams 1991; Hesslin 1976; Mayer 1976; Carignan and Lean 1991; Bufflap and Allen 1995ab; Carignan 1984; Bottomley and Bayly 1984; Sarda and Burton 1995; Teasdale *et al.* 1995, 1996; Chappie and Burton 1997; Davison *et al.* 1991) or *in situ* suction techniques (*e.g.*, Knezovich and Harrison 1987; Howes *et al.* 1985; Whitman 1989; Watson and Frickers 1990). Peepers (diffusion samplers) have been used in the development of sediment metal guidelines (*i.e.*, the AVS approach) in laboratory sediment spiking experiments (Berry *et al.* 1996). These methods have the greatest likelihood of maintaining *in situ* conditions and have been used to sample dissolved gases (Barnes 1973; Sarda and Burton 1995) and volatile organic compounds (Knezovich and Harrison 1987). These techniques, however, isolate only relatively small volumes of pore water, and in deeper waters, must be placed by divers which limits the depth and conditions at which the devices can be deployed. *In situ* suction of undisturbed sediments is also possible from sediments collected by box core or grab samplers, or by insertiion of air stones (as discussed in the previous section).

The duration of equilibration for peepers, where pore waters diffuse through dialysis to mesh membranes, have ranged from hours to a month, but one to two weeks is most often used (Adams 1991; Teasdale *et al.* 1995). The optimal equilibration time is a function of sediment type, contaminants of concern, and temperature (*e.g.*, Howes *et al.* 1985; Simon *et al.* 1985; Bottomley and Bayly 1984; Carr *et al.* 1989; Skalski 1991; Fisher 1991). Recently, Webster *et al.* (1998) showed the rates of peeper equilibration of several inorganic ions in marine sediments and developed a computer model to show the effect of peeper design and placement. Equilibration was affected by peeper volume, ion type, peeper position, surrounding medium (water vs. sediment), and membrane area. Equilibration times (using a 0.45 µm membrane) ranged from 9 to 90 days in sediments and only hours in waters. The rates of equilibration were seen as worst case (slowest), as they were based on molecular diffusion only.

There are several artifact problems associated with peepers that use dialysis membranes (Carignan *et al.* 1985). Total organic C may be elevated in peepers (4 to 8 µm pore size) due to biogenic production; however, colloidal concentrations are lower than centrifuged samples (Chin and Gschwend 1991). Cellulose membranes are unsuitable as they decompose too quickly. A variety of polymer materials have been used, some of which may be inappropriate for studies of certain nonpolar compounds. Polysulfone membranes are more resistant to biofouling (Teasdale *et al.* 1995). More recently, larger pore-sized mesh has been used which allows faster equilibration (Sarda and Burton 1995). Solids passing through larger mesh tend to settle to the bottom of the peeper chamber. Peeper chamber lengths have ranged from a few cm to over 1 m.

Peepers are effective tools for measuring pore water flux of metals using multidepth samplers. Redox gradients with associated Fe oxyhydroxides and metals complexation have been shown over several cm depths of sediments (Tessier *et al.* 1989; Teasdale *et al.* 1996). This is of significance as it can document the dissolution of sulfide-metal and oxyhydroxide complexes and their upward diffusion into overlying waters (Teasdale *et al.* 1996). Diffusional fluxes may be calculated using Fick's first law (Lerman and Brunskill 1971; Ulman and Aller 1982) by knowing the concentration gradient at the sediment water interface and sediment tortuosity corrections are made (Berner 1980; Nyffeler *et al.* 1984; Teasdale *et al.* 1996).

When ionizable compounds, (*e.g.*, metals) are to be collected, it is important to pre-equilibrate the samplers with an inert atmosphere to avoid introducing oxygen into the sediments and thereby changing the equilibrium. Plastic samplers can contaminate anoxic sediments with diffusable oxygen and should be stored before testing in inert atmospheres (Carignan *et al.* 1994). In addition, when samples are collected and processed, they should also be kept under an inert atmosphere and processed quickly.

Peepers have been tried successfully at two sites receiving mining discharges (ENSR 1997; Teasdale *et al.* 1996). A detailed assessment was conducted in an Australian harbor and delta to assess the fate of Cu in the sediment and associated pore water. Through the use of water and sediment chemistry and peeper analyses, they quantified the flux of Cu into and out of the sediments from freshly deposited to aged sediments ranging from high to low contamination (Teasdale *et al.* 1996). This allowed the development of a model showing sediment cycling in each subsection of the study area, as defined by hydrologic and physicochemical characteristics (Teasdale *et al.* 1996). Unfortunately, biological assessments were not included in this study.

On the Clark Fork River, an extensive ecological risk assessment has been conducted (Pascoe and DalSoglio 1994; Pascoe *et al.* 1994). Whole sediments and pore waters were characterized chemically (including AVS) and extremely high spatial variability was found (Brumbaugh *et al.* 1994). Pore water toxicity was measured using *Daphnia magna* (48 hr), rainbow trout (96 hr) and Microtox® (Kemble *et al.* 1994). Changes in pore water chemistry were noted after 5 to 7 d storage. A flocculation of material occurred within the first 24 hr of pore water exposures, indicating Fe and Mn oxyhydroxide precipitation. They recommended toxicity testing within 12 to 24 hr of collection. Whole sediment tests (*Hyalella azteca* and *Chironomus riparius)* were more sensitive than pore water tests. A sediment quality triad approach showed strong correlations between benthic invertebrate communities, pore water metal concentrations, and laboratory toxicity (Canfield *et al.* 1994). Laboratory exposures of the amphipod *Hyalella azteca* showed 50 to 75% less bioaccumulation of As, Cd, Cu, Pb, and Zn than field-collected invertebrates (Ingersoll *et al.* 1994). Follow-up work including pore water peepers was used to determine: the relationships among metal concentrations in whole sediments, pore water and overlying water; the relationships among chemical and biological endpoints; and sediment and pore water quality. High metal concentrations were observed in depositional sediments; however, there was no significant correlation between pore water and depositional sediment metals concentrations and any benthic macroinvertebrate measured responses. There was, however, a correlation between pore water metals in riffle sediments and overlying waters. This would be expected since there is significant pore water exchange in coarse-grained riffle habitats. In these areas, no biological effects were observed, as predicted based on a summation of metal toxic units in the water. These peeper studies confirmed that depositional sediment metals were not biologically available (ENSR 1997).

Metals sampling of pore waters can be accomplished using a polyacrylamide gel probe (Krom *et al.* 1994, Davison *et al.* 1991; Davison and Zhang 1994). These probes consist of an ion exchange resin overlain with an ion permeable gel (DET) with short equilibration times. Pore water concentrations can be measured via diffusional equilibration or a kinetic diffusion gradient analysis.

Microelectrodes have been used to directly measure pore water pH, CO_2, O_2 and H_2S (Carlton and Klug 1990; Cai and Reimers 1993; Brendel and Luther 1995; Revsbech *et al.* 1983; Visscher *et al.* 1991). Additionally, semipermeable membrane devices (SPMDs) filled with a non-polar sorbant have been effectively used to show potential for bioaccumulation of nonpolar organic compounds. These last 3 approaches (gel probes, microelectrodes, and SPMDs) have not been widely used or thoroughly documented as being useful for metals bioavailability testing.

Finally, *in situ* sampling of metals has been successful by inserting Teflon™ or polycarbonate strips which adsorb diagenetic Fe and manganese oxyhydroxides, AVS and associated trace metals (De Vitre *et al.* 1991; Teasdale *et al.* 1996; Belzile *et al.* 1989; Huerta-Diaz *et al.* 1993; Tessier *et al.* 1996). Over a period of weeks, the oxygen within the strip leads to deposition of hydrous Fe oxides on the Teflon™ strip which then slowly retracts as excess sulfide diffuses over the oxygen and reaches *in situ* equilibrium conditions. An As study in Canadian Shield lakes using Teflon collectors showed arsenite was oxidized by Fe oxyhydroxides to arsenate, with field-derived equilibrium constants agreeing with laboratory constants. The oxidation of As is also enhanced on kaolinite and illite clay surfaces (Manning and Goldberg 1997). This is important from a biological perspective because arsenate associated with Fe oxyhydroxides is less toxic than arsenite.

Recently, test organisms have been exposed within peeper chambers where larger mesh sizes of 149 µm were used successfully in oxic sediments (Fisher 1991). Equilibration of conductivity was observed within hours of peeper insertion into the sediment (Fisher 1991). Replicate peepers revealed extreme heterogeneity in sediment pore water concentrations of ammonia and dissolved oxygen (Frazier *et al.* 1996; Sarda and Burton 1995; Sherman *et al.* 1994). Sediments high in clay and silt fractions usually were anoxic and did not allow for organism exposure *in situ* (Fisher 1991).

As discussed above, there is no one clearly superior method for the isolation of pore water for toxicity testing purposes. Each approach has unique strengths and weaknesses which vary with the sediment's characteristics, the contaminants of concern, the toxicity test methods to be employed, and the resolution necessary (*i.e.*, the data quality objectives) (Table 2). There are a number of precautions that should be taken to reduce the likelihood of causing significant sample alterations from *in situ* conditions. For some toxicity test procedures, relatively large volumes of pore water (*e.g.*, liters) are frequently needed for static or static renewal exposures with the associated water chemistry analyses. However, effective toxicity testing is possible with smaller volumes by testing without dilution, on a microscale, with multiple species per test beaker, and/or without renewals. In general, it is not necessary to determine an EC50, when a simple indication of whether the whole pore water sample is toxic is the study objective. If smaller volumes are adequate and logistics allow, the use of *in situ* methods is preferred, as they are less likely to produce sample artifacts. If logistics do not allow placement of *in situ* samplers, then the collection of core samples subjected to immediate side port suctioning or centrifugation at ambient bottom water temperatures is recommended. For most studies, however, it will be necessary to collect larger quantities of samples, preferably multiple cores, which are processed in an inert environment and centrifuged at ambient temperatures as quickly as possible.

Table 2. Optimal *In Situ* Pore Water Collection Methods

Device	*Sediment Depth (cm)*	*Volume (cm^3)*	*Advantages*	*Disadvantages*
Peeper	0.2 - 10	1 - 500	Most accurate method, reduced artifacts, no lab processing; relatively free of temperature, oxidation, and pressure effects; inexpensive and easy to construct; some selectivity possible on nature of sample via specific membranes, wide range of membrane/mesh pore sizes, and/or internal solutes or substrates	Requires deployment by hand, thus requiring diving in > 0.6 m depth waters; allow hrs to days for equilibration which will vary with site and chamber; methods not standardized and used infrequently; some membranes such as dialysis/cellulose are subject to biofouling; must deoxygenate chamber and materials to prevent oxidation effects; some chambers only allow small sample volumes; care must be used on collection to prevent sample oxidation
In situ Suction collection devices	0.2 - 30	1 - 250	Reduced artifacts, gradient definition; shallow water (<0.6m) method ease; core method may not require diving in deep waters; water, rapid collection, no lab processing; closed system which prevents contamination possible; methods include airstone, syringes, probes and cores	Requires custom, non-standard collection devices; small volumes; limited to softer sediments; core airstone method may require diving for deployment in deep waters; methods used infrequently and by limited numbers of laboratories
Centrifugation	Sampler dependent		Most accurate of lab processing methods; allows anoxic/cold processing; large volumes; commonly used	Some chemical loss/alteration; results depend on centrifugation conditions; requires high speed centrifuge; difficult with sandy sediments
Suction	Sampler dependent		Use with all sediment types; may process in field; large volumes possible with some sediments; closed system possible	Alteration of chemical characteristics may occur; increased loss of metals and organics; loss of vertical gradient resolution
Squeeezing	Sampler dependent		Use with all sediment types; may process in field; large volumes possible with some sediments; closed system possible	Alteration of chemical characteristics may occur; increased loss of metals and organics; loss of vertical gradient resolution

Note: Incorporation of filtration into any of the collection methods may result in loss of metal and organic compounds.

2.4.2. Storage

Toxicity changes have been observed in pore water stored for short periods. Coagulation and precipitation of the humic material was noted when pore water was stored at 4°C for more than one week (Landrum *et al.* 1987). Oxidation of reduced As species in pore water of stored sediments was unaffected for up to 6 weeks when samples were acidified and kept near 0°C, without deoxygenation. When samples were not acidified, deoxygenation was necessary (Aggett and Kriegman 1987). Others have recommended pore waters be frozen after extraction, prior to toxicity testing, to prevent changes in contaminant state (Carr *et al.* 1989). Ammonia decreased significantly in pore water stored at 4°C at 2 weeks, with acid preservation (Sarda and Burton 1995).

2.5. Cost Effectiveness of Pore Water Testing

2.5.1. Availability and Cost of Commercial Testing

A large number of laboratories were surveyed (Table 1) about pore water testing. It was interesting that the responses were uniformly similar, despite the wide geographical and job sector range. All responded that very little pore water toxicity or chemistry testing was being conducted. However, all had done some pore water testing and were very capable of performing high quality analyses. This was evidenced by their awareness of critical issues regarding chemical and toxicity alteration from sample manipulation. A general concern was the lack of standardization and ring (round robin) testing of pore water extraction procedures. The laboratories all stated that a significant issue was the collection of adequate quantities of pore water for analyses. If one did not collect enough sediment (not knowing the pore water content *a priori*) then resampling may be required which may be expensive or not possible. Another issue was the added cost incurred due to the pore water extraction procedure. Most laboratories used the preferred method of centrifugation to isolate pore water, however, several did not have large refrigerated high speed centrifuges which greatly increased time for isolation of adequate test volumes. The average time involved in pore water isolation was 0.5 hrs at approximately $50 (US and Canadian)/hr charge. Some sediments require double centrifugation to remove clays or obtain additional pore water. This cost was added to the routine cost of toxicity testing for conventional test species such as *C. dubia, P. promelas, H. azteca, C. tentans, Selenastrium capricornutum* microplate or traditional, Microtests (*e.g.*, Rototox®) and Microtox®. Microtox® testing, being done frequently by British Columbia Ministry of Environment, is the least expensive assay ($50 to $60 Canadian) with other assays costing from $400 to $600 (Canadian). However, some high end tests could cost as much as $1,200 (US) for definitive serial dilution testing. Microtox® has also been somewhat controversial from an ecological significance and sensitivity perspective (Burton *et al.* 1996). Another advantage of the micro-tests is that they require small volumes of pore water (*e.g.*, 20 to 30 mL); while the sea urchin test requires 100-500 mL and the algal growth test 100-200 mL if full serial dilution tests were to be conducted. However, if, for example, a *Ceriodaphnia* single concentration test were conducted as per Environment Canada test methods, with 3 replicates, test solution requirements would only be 45 mL. The U.S. EPA draft sediment Toxicity Identification Evaluation (TIE) procedures (U.S. EPA 1991abc) expose *Ceriodaphnia* to only 10 mL quantities of pore water. Single concentration testing could make pore water testing with more traditional test organisms more feasible.

The costs for constructing *in situ* pore water collection devices, such as “peepers”, varies widely. The simpler plastic chambers which have mesh or membrane “windows” are relatively simply to construct and use inexpensive materials. Cost will vary with the quantity and amount of labor, but should range from $25 to $100 each. Sampling devices which are constructed of stainless steel or polymers such as polytetraflouroethylene (PTF) and which allow remote deployment and suction can be expensive, but may be necessary in some extreme environments.

2.5.2. Data Interpretation

Data interpretation is relatively straightforward for toxicity testing. If organisms are killed or inhibited in the assay at a statistically significant level compared to controls and/or reference samples, then a detrimental effect can be attributed to the test sample. Guidelines which state that 50% or 25% inhibition are appropriate criteria are not based on the carrying capacity of the ecosystem. Any such criteria should be a site specific decision, as each ecosystem varies in its ability to handle stressors. Data are best interpreted in a weight-of-evidence approach as discussed in the Introduction.

The chronological steps to consider when designing a sediment and pore water collection plan in a metal bioavailability study are as follows:

1. Determine sediment type
    Fine-grained or coarse-grained
    Compacted or non-compacted
2. Determine sediment and/or pore water volume needed and contaminants of interest (regarding effect of oxidation): (If unknown, assume pore water cannot be collected from compacted sediment. Assume non-compacted sediment is 25% water, minimum.)
3. Choose optimal whole sediment sampler (See also No. 7 if pore water to be collected)
    Consider sediment type
    Consider sediment volume needed

Consider sampling logisitics such as: water depth, temperature, potential for hand collection or placement of samplers, sampling equipment and sampling vessel available

Choose appropriate sampler, in order of preference:

1. *In situ* peeper
2. *In situ* suction
3. Core
4. Grab
5. Dredge

4. Process sample in anoxic conditions, unless study objectives warrant otherwise

5. Maintain sample at 4°C.

6. Analyze whole sediment sample as soon as possible (2 weeks maximum unless adequate justification provided). Do not store pore water for longer than 48 hrs.

7. Collect pore water (in order of preference; see also No. 3)

   1. *In situ* peepers
   2. *In situ* suction (air stone or core-port)
   3. Centrifugation @ 10,000 x g (4°C) (without subsequent filtration)
   4. Centrifugation @ lower speeds
   5. Basal cup
   6. Squeezing or pressurization
   7. Suction or filtration

Theoretical Case Example 1:

A site was sampled in January with depositional sediments (unconsolidated silts and clays), and was ice-covered with water depths of 15 to 20 m. Site conditions prevented use of peeper sampling and no *in situ* core-port sampling equipment was available. The study design required collection of 30 L of sediment. Based on these restrictions, a Ponar grab sampler was the most appropriate for sediment collection.

Replicate ponar grabs were deposited into a 20-L high density polyethylene bucket and gently stirred to homogenize. Nitrogen gas was bubbled into any overlying water and added to the head space prior to lid closure. Sediments were placed in ice chests at approximately 4^0C and returned to the laboratory for processing.

Pore waters were collected using centrifugation. Sediments were distributed to the appropriate type of centrifuge bottles under a nitrogen atmosphere and centrifuged at 10,000 x g at 4^0C for 30 minutes. The supernatant was gently decanted under a nitrogen atmosphere. The study team was aware that if solids were resuspended with the supernatant, a second centrifugation of the pore water would be conducted. The pore water from all bottles was combined under nitrogen and then split for chemical analyses and toxicity testing. Chemical samples were preserved and stored as appropriate. Toxicity testing was initiated within 48 hrs at which time the sample temperature was raised from 4^0C to the required test temperature and dissolved oxygen checked to ensure adequate levels exist. Water quality testing during the bioassays showed high initial concentrations of ammonia, which decreased to nontoxic levels within 48 hrs. Bioassay results showed toxicity existed, but was lost when testing was repeated on stored pore water samples. Subsequent chemical analyses showed an SEM:AVS<1 indicating metals were likely not contributing to toxicity. These results suggested that toxicity was due to ammonia.

Theoretical Case Example 2

A shallow stream with sediment contamination was studied to develop site-specific sediment quality criteria. Site conditions allowed the placement of peeper samplers. The sediment depth of concern was from 0 to 5 cm. Peepers were constructed from high density polyethylene bottles with 70 to 140 µm PTF mesh windows on the chamber walls, 1 to 5 cm from the top of the chamber. Chambers were filled with sterile deionized water and placed in a nitrogen atmosphere for 24 to 48 hrs prior to site placement. Five replicate (total volume approximately 2.5 L) chambers were placed at the site by removing a plug of sediment (of similar size to the chamber), inserting the chamber into the sediment, and gently packing the sediment around the chamber so that only the lid was exposed. Equilibration time was reduced due to the large mesh size on the chamber and the sandy nature of the sediment. Time series sampling of the pore water was possible by constructing an outlet tube into the chamber lid to which tygon tubing was attached and clamped off (Sarda and Burton 1995). Pore water was sampled by attaching a degassed 50 mL syringe to the outlet tube and withdrawing pore water. This provided a pore water sample without disrupting the chamber or sediments. Equilibration time for major ions in the pore water of the sandy sediments occurred within several hours. However, it may require several days for the sediment gradients adjacent to the peeper to reestablish after initial disruption. Sampling of pore waters at the sediment surface (0 to 1 cm depth) was not readily feasible due to the need for larger pore water samples. However, toxicity was determined on surficial sediment using *in situ* toxicity test chambers exposing organisms either directly to the sediments or via mesh barriers (Burton 1992). Micro-analytical sampling of near surface sediments was possible using narrow plate chamber designs (see reviews in Adams 1991, Burton 1991, and above citations). Samples were sent to the laboratory on ice and then processed by the appropriate chemical and toxicity test methods.

Results showed that high mortality in organisms exposed at the sediment water interface in the zones of highest contamination. Chemical analysis of surficial sediments and water from *in situ* toxicity test chambers showed high levels of metals associated with sediments, but not overlying waters. Peeper sampling also confirmed metals concentrations in surficial pore waters that exceeded AVS concentrations. Based on these results, metals were identified as the likely stressor and a site-specific criteria established by comparing with sites where lower contamination and toxicity was observed.

3.0. Assessments of Whole Sediments Using Total and Selective Extractions

3.1. Overview of Methods and Critical Issues

Various methods have been recommended to determine bioavailable fractions of metals in sediments (Di Toro *et al.* 1991). One extraction procedure, cation exchange capacity, provides information relevant to metal bioavailability studies. Amorphous oxides of Fe and manganese, and reactive particulate C have been implicated as the primary influences on metal sorption potential in sediments (Jenne and Zachara 1987; Crecelius *et al.* 1987; Jenne 1968, 1977, 1987). Measurement of AVS and divalent metal concentrations associated with AVS extraction provides insight into metals availability in anaerobic sediments (Di Toro *et al.* 1991). Easily extractable fractions are usually removed with cation displacing solutions, for example, neutral ammonium acetate, chloride, sodium acetate, or nitrate salts (Lake *et al.* 1984). Extraction of saltwater or calcareous sediments, however, is often complicated by complexation effects or dissolution of other sediment components (Kersten and Förstner 1987; Maher 1984). Other chemical extractants of sediments and associated advantages and disadvantages have been discussed (Kersten and Förstner 1987; Jenne 1987; O'Donnel *et al.* 1985; Salomons and Förstner 1984). Some extractants that have been successfully used in evaluations of trace metals in nondetrital fractions of sediments are EDTA or HCl (Kersten and Förstner 1987). Metal partitioning in sediments might be determined by using sequential extraction procedures that fractionate the sediments into several components such as pore water, ion exchangeable, easily reducible organic and residual sediment components (Engler *et al.* 1977; O'Donnel *et al.* 1985; Khalid *et al.* 1981; Tessier *et al.* 1979). Unfortunately at this time no one method is clearly superior to the others (Maher 1984). This might be due, in part, to site specific characteristics which influence bioavailability (*e.g.*, desorption and equilibration processes).

3.2. Total and Near-Total Metal Analyses

Metals can be extracted from sediments in a number of ways, with acid digestions being used for total and near-total extractions. Obtaining total concentrations requires dissolving of silicate lattices, releasing tightly bound metals and is most effectively accomplished with hydrofluoric acid (HF) (Loring and Rantala 1992). Due to the expense and safety concerns of using HF, near total digestions are more frequently done with nitric acid, perchloric acid or sulfuric acid (or mixtures thereof). A popular "near total" digestion utilizes *aqua regia* (i.e., 3:1 mixture of HCl and HNO_3). *Aqua regia* and 0.5 M HCl have been compared to HF in extraction efficiency and found to be similar to Pb and Zn and quite different with Cr. Cd and Cu results varied. Sediments with high silicate content will tend to Pb to greater differences between weak and strong digestions (Loring and Rantala 1988). The choice of which acid(s) and digestion condition to use varies widely. Any method using these concentrated acids during rigorous digestions will release near total concentrations, and may greatly exceed the bioavailable (easily extractable) fractions. Luoma and Bryan (1978) showed deposit feeding bivalve uptake of Pb could be predicted from the Pb/Fe ratio in 1 N HCl extracts of surface sediments, and this extract is superior to five other extraction methods (Luoma and Bryan 1982).

3.3. Selective Extractions

There is a long history of the use of selective extractions to determine the bioavailability of chemicals attached to soil and sediments. A wealth of agricultural and soils literature exists dealing with metal, metalloid, and nutrient availability. Many of these studies related the "easily extractable" fractions with plant uptake. Extracting solutions were typically dilute solutions of HCl or ammonium acetate. The classic works of Tessier and Patrick and many others have shown the usefulness of sequential extractions of sediments for determining the binding affinity of metals (*e.g.*, Tessier *et al.* 1979; Salomons and Förstner 1980; Loring and Rantala 1992; Patrick 1964, Brannon *et al.* 1976).

There are many variations of the selective extraction approach; however, all are similar in that a sequential series of increasing strong solutions are used to extract metals from sediments ranging from easily extractable to residual binding phases. The four major phases can be categorized as follows: Adsorption and cation exchange, carbonate phases, reducible phases, and organic fractions (including sulfides) (Tessier and Campbell 1987). The chemical extractants include concentrated inert electrolytes, weak acids, reducing agents, complexing agents, oxidizing agents and strong mineral acids . The procedures are designed for use with oxic sediments (Tessier and Campbell 1987) but have been used in anoxic environments (Brannon *et al.* 1976). Specific selectivity deteriorates with increasing sulfide content (Campbell and Tessier 1984; Rapin *et al.* 1986) and drying and other pretreatment methods have marked effects (Tessier and Campbell 1987). Trace metals may occur in several extractable phases: particle surfaces (*e.g.*, clays, humics, oxyhydroxides); carbonate bound; occluded in Fe or manganese oxyhydroxides; bound in organic matter; sulfide bound; or matrix bound (*e.g.*, in aluminosilicates) (Tessier and Campbell 1987). The problem usually associated with the sequential extraction procedures is some lack of selectivity, particularly with recently formed sulfides. In addition, readsorption of metal to remaining solids may occur during the extraction process. These issues have been thoroughly discussed (Tessier and Campbell 1988, 1991; Nirel and Morel 1990). Recently, a nitric acid extractable phase was shown to be effective in a bioavailability study in Brazil (Perin *et al.* 1997). The strongest complexation influence was hydrogen sulfide in highly reduced environments. Metal partitioning based on selective extractions will vary depending on the reagents used, extraction methods, and solid/extractant ratio.

Of particular importance is the way sediments are initially processed and/or preserved, such as air drying, freeze drying, freezing, or wet storage at 4^0C. Many of the problems are associated with use of artificial sediment, where trace elements are present as a single phase and not representative of more complex natural sediment complexations. However, their usefulness has been well documented (Fitzgerald *et al.* 1987; Luoma 1989; Hare 1992).

Simultaneous extractions have been used with substitution of various chemicals for the exchangeable fraction (Singh *et al.* 1984; Bendell-Young and Harvey 1992). While many selective extractions of more easily exchangeable fractions have been successfully related to tissue concentrations, they currently cannot be used routinely as predictors of metal availability due to the many associated uncertainties discussed above (Luoma 1989). As our understanding of the mechanistic processes involved in these methods improves, then so will their usefulness for routine applications.

British Columbia has a standard method for extracting contaminants from solid wastes (British Columbia Regulation No. 63/88 1994). This Solid Waste Extraction Process (SWEP) is a modified leachate extraction procedure. Any pore water is removed from the sample via filtration. Then reagent water (800 mL) is used to extract the solids (50 g) by mixing for 1 hour, then diluting to 1 L. The supernatant is then removed and analyzed. This approach is utilized by the BC Ministry of Environment for liquid testing of sediments using Microtox®, *Daphnia magna*, and *Selenastrum capricornutum* microplate assays (G. van Aggelen, personal communication, 1998).

Elutriate Preparation: Many studies of sediment toxicity have employed aqueous extractions of suspended sediment called elutriates (Ankley *et al.* 1991; Chapman and Fink 1984; Ross and Henebry 1989). The method of elutriation was originally to simulate processes that might disturb the sediment and thus bring contaminants into the water column, i.e., dredging activities developed (U.S. Army Corps of Engineers (1976). The method has been further adapted to evaluate the effects of other common events that disrupt sediments and affect water quality such as bioturbation and storms (Burgess *et al.* 1993). Elutriates are generally prepared by combining various mixtures of water and sediment (usually 4:1 ratio, v/v) and shaking, bubbling or stirring the mixture for 1 h (Burgess *et al.* 1993; Ankley *et al.* 1991; Ross and Henebry 1989; Daniels *et al.* 1989). The water phase is then separated from the sediment by centrifugation and the supernatant is used in various toxicity tests (*e.g.*, fathead minnow, *Pimephales promelas*; bioluminescence assay, *Photobacterium phosphoreum (Vibrio fischeri)*; sea urchin (*Arbacia punctulata*) fertilization test, bivalve larval test). Filtration of the supernatant through filters (0.45- to 1.2 μm) may be necessary when the elutriate is used in some toxicity tests such as the algal growth assay with *Selenastrum capricornutum*. However, as discussed in previous sections, filtration can remove toxicity due to sorption of dissolved chemicals to the filtration membrane and retention of colloids. In general, elutriates have been found to be less toxic than bulk sediments or pore water fractions (Burgess *et al.* 1993; Ankley *et al.* 1991) to various biota but there have been isolated cases where resuspension increased the bioavailability of toxicants in the water column. Partitioning to organic colloids in the pore water has been suggested as a possible explanation for the discrepancies between suspended-phase and interstitial water exposures (Burgess *et al.* 1993). Harkey *et al.* (1994) found elutriates or extracted pore waters did not predict sediment bioavailability of organic contaminants in sediments. Toxicity may be significantly affected by the method of elutriation; therefore, data comparisons should only be made where standardized elutriate methods were used.

The AVS approach has received the support of the U.S. EPA for the development of metal criteria for sediments. A large number of studies have verified the usefulness of this approach (Berry *et al.* 1996; Di Toro *et al.* 1990, 1992; Carlson *et al.* 1991; Casas and Crecelius 1994; Green *et al.* 1993; Pesch *et al.* 1995; Ankley *et al.* 1991, 1996ab; Hansen *et al.* 1996ab; De Witt *et al.* 1996; Sibley *et al.* 1996; Hare *et al.* 1994; Liber *et al.* 1996). As discussed earlier, it has been field validated with Cd and Ni but does not always predict Cu toxicity or other metals. When the molar ratio of SEM:AVS exceeds one then acute toxicity due to the metal may occur, as the AVS binding capacity is exceeded. However, when the ratio is less than one, acute toxicity is rarely observed (Ankley *et al.* 1996b). Cu shows better correlations with toxicity using organic C concentrations for normalization. It is primarily the dissolved organic C fraction that controls Cu availability. Other ligands, such as organic C, may reduce or increase the bioavailability of the metals in the pore water. At low pH, metal ion activity is increased and may not follow the AVS/SEM model.

Recently, Simpson *et al.* (1998) conducted mechanistic studies on oxidation rates of model metal sulfide phases. They found FeS and MnS phases were very labile and oxidized rapidly while CdS, CuS, PbS and ZnS were stable for several hours. If sediments were resuspended for more than 5 hrs, AVS decreased lower than SEM values. SEM Cu was found to increase more than the other metals and was an artifact of the AVS/SEM procedure. This is another factor which suggests caution should be used with Cu and AVS predictions. The studies to date have largely focused on acute toxicity and not bioaccumulation (Besser *et al.* 1996).

In the most commonly used AVS method, a 1M cold HCl solution is used to extract the sulfide and its associated metals (Allen *et al.* 1993). Various conventional methods can then be used, such as colorimetric, gravimetric, gas chromatographic and ion electrodes. Simpson *et al.* (1998) recently showed the limitations of the AVS extraction procedure. Oxidation of AVS during collection and sample manipulation can lead to erroneous results (Zhuang *et al.* 1994).

Gonzalez (1996) recently developed a formulated sediment containing AVS with potential applications for quality control documentation.

3.4. Pore Water Measurements

A variety of analytical methods exist for measuring metals in pore waters, some of which are useful for speciation of metals. Each method has associated weaknesses, however, and often cannot be used to determine metal speciation reliably. The measurement of methylmercury compounds was conducted efficiently using equilibrium dialysis (Hintelmann *et al.* 1997). The authors showed that methylmercury (II)-HS complexes dominate in oxidized freshwaters with low sulfide concentrations, while CH_3HgSH prevails in anoxic waters (such as pore waters of depositional sediments). The CH_3HgCl complex was too weak to compete with either of these above complexes.

3.5. Relationship Between Sediment Chemistry and Biological Effects

In cases where significantly high levels of toxic nonpolar or metal contamination exist in sediments, there are strong relationships between concentrations and biological responses. However, for every site where gross contamination exists, there is a gradient where moderate levels of chemicals exist. At the moderately contaminated sites, the relationship between contaminant concentrations and biological quality is less clear.

A wide range of success stories exist in the literature regarding the correlation between various sediment extracted components and biological responses. Some of these involve strong acid extractions (Luoma and Bryan 1978, 1982) of metals being related to tissue metal concentrations, as were concentrations of Fe, manganese, humic acids, carbonates or total organic C (Tessier and Campbell 1987). Iron and manganese oxides were shown to be more important than organically-bound metals in tubificids (Andrews and Fitchko 1987). Manganese oxide-associated Cu was 100 times more bioavailable than Fe associated Cu oxides (Luoma and Jenne 1977). It is apparent from these and other studies that the route of exposure and uptake varies with site characteristics and the species (*e.g.*, Luoma 1989; Tessier and Campbell 1987; Burton 1991). Understanding the partitioning of trace metals in oxidized sediments is very important to determine whether the environment is safe for aquatic organisms (Luoma and Davis 1983). Tessier *et al.* (1993) modeled Cd partitioning in oxic lake sediment and in a freshwater bivalve using an integrated assessment. Using peepers, Teflon strips, and traditional water and sediment chemistry with bivalve exposures, they constructed accurate predictions of Cd availability. Surface complexation concepts of binding intensity for sorption of Cd to Fe oxyhydroxides and organic matter were estimated from field data following lake pH. These relationships showed Cd was mainly bound to organic matter in the site sediments. By combining surface complexation values with the free-metal ion model, they predicted Cd tissue concentrations and dissolved Cd from water pH and sediment chemistry. Benthic macroinvertebrate population effects varied greatly in Cd contaminated sediments where the Cd:AVS molar ratio exceeded one. Only one species of *Chironomus* was affected. The authors suggested this lack of affect was likely due to varying species sensitivity and low levels of excess Cd (Hare and Shooner 1995; Hare *et al.* 1994). Morrisey *et al.* (1996) also showed population differences in Cu contaminated sediments with a significant degree of spatial and temporal variation. Perhaps the single most important factor for determining whether a population of organisms is susceptible to metal toxicity is its exposure, which can only be determined by knowing where the organism lives and how it feeds (Hare *et al.* 1998).

Organisms have been shown to adapt to metal exposures. *Chironomus riparius* larvae developed acclimation-based resistance in long term exposures to Zn (Miller and Hendricks

1996). This phenomenon may account for some of the differences noted between laboratory bioassay results and indigenous populations.

The spatial and temporal variation of AVS has been well documented (Besser *et al.* 1996; Howard and Evans 1993). Surficial sediments containing higher levels of AVS than deeper sediments were less toxic. Copper bioaccumulation and effects were affected by AVS levels, however, Zn was not (Besser *et al.* 1996). AVS was shown to have a seasonal trend, peaking in spring and fall and being highest in mid-lake (profundal) sediments where natural organic loading was highest (Howard and Evans 1993). This is due to the S loading from decaying organic material. Changes in reduced sulfur species of greater than an order of magnitude were observed in salt marsh sediment pore waters during some seasons, but little change was observed in other years (Luther *et al.* 1991).

Fortunately, in the past couple of years, there has been a tremendous increase in the size of databases dealing with sediment quality chemical guidelines and biological responses. Several investigators have conducted extensive evaluations of the effectiveness of different sediment quality guidelines (Ingersoll *et al.* 1997; McDonald *et al.* 1996; Long *et al.* 1995). Most of these relationships are based on total chemical (nonpolar and metal) concentrations which are normalized to TOC (nonpolar organics) and AVS (metals). When AVS is not known then total metal concentrations are used, which is usually the case. Despite the drawbacks already discussed in using total metal concentrations, the Effect Range Medium and Effect Range Low (ERM/ERL) and Probable Effect Limit and Threshold Effect Limit (PEL/TEL) guidelines of Long and Morgan, and McDonald, respectively, show a high degree of accuracy, with only approximately 10% false positive and negatives reported (Ingersoll *et al.* 1997). However, it is apparent that the database and accuracy for some metals is less than desirable, such as Ni, and that site specific conditions must be considered. Recently, Long *et al.* (1998) showed that the effectiveness of predicting sediment toxicity by normalizing to sediment dry weight was equally or slightly more accurate in predicting both nontoxic and toxic results in laboratory tests relative to SEM:AVS concentrations.

Environment Canada is producing sediment quality guidelines for many metals, including: Cd, Hg, As, Cr, Cu, Pb, Zn, Ni and Ag. These guidelines are based on the modified National Status and Trends Program (NSTP) and the Spiked-Sediment Toxicity Test approach. Most interim guidelines are based on Threshold Effect Levels (TELs) and Probable Effect Levels (PELs) using the modified NSTP approach.

The National Research Council of Canada produced a comprehensive review with recommendations entitled "Biologically Available Metals in Sediments" (Campbell *et al.* 1988). The report covered a number of important issues including: 1) factors affecting metal geochemistry, biological effects and predictions, geochemical predictions of bioavailability, and biological monitoring. It is of interest that the conclusion of the report still applies today:

"...metal bioavailability should be estimated not by a single technique but through a combination of geochemical assays, bioassays and biochemical monitors. Each of these provides information that must be considered collectively to provide the best estimate of bioavailability. Furthermore, it is essential that the biologist and the geochemist combine their efforts if we are to truly understand the biological importance of metals in sediments."

3.6. Background Concentrations

It is useful to evaluate metal contamination by comparing sediment and soil metal concentrations to "background" or "ambient" levels. Environment Canada has defined "background" as: Estimates of naturally-occurring concentrations (i.e., no discernable human influence on measured concentrations). "Ambient" concentrations are defined as: Concentrations that are generally typical of (or represent "baseline" conditions for) a given area and may be the result of human activities, natural processes, or both (*i.e.*, this evaluation could not conclusively identify these data as either "background" or "contaminated" but they likely have at least some anthropogenic component). Environment Canada has done an extensive literature survey of metal concentrations across the country on metals for which sediment quality guidelines are being developed. Background and ambient concentrations vary widely across Canada and within geologic regions (Environment Canada 1996). However, by determining a local reference value (background or ambient) then "contamination" gradients can be reasonably defined by comparing to the reference value. This ratio will not provide information on bioavailability, but can help direct further assessment activities.

3.7. Sediment Sample Collection and Manipulation Issues

Maintaining the integrity of a sediment sample relative to its condition in the natural environment during its removal, transport, and testing in the laboratory is extremely difficult. The sediment environment is composed of a myriad of microenvironments, redox gradients, and other interacting geo- and physicochemical and biological processes. Many of these characteristics influence contaminant bioavailability and subsequent toxicity to benthic and planktonic organisms, microbial degradation, and chemical sorption. Any disruption of this environment complicates interpretations of treatment effects, causative factors, and *in situ* comparisons.

Whole sediment and pore water toxicity and bioaccumulation tests are meant to serve as indicators of contaminant-related toxicity and bioavailability that might be expected under field or natural conditions. Although the tests are not designed to simulate natural conditions, there is concern that contaminant availability in the test is different from what it was in nature. Sediment collection, handling, and storage may alter contaminant bioavailability and concentration by changing the physical, chemical, or biological characteristics of the sediment. These manipulation processes are generally thought to increase availability of organic compounds because of disruption of the equilibrium with organic C in the pore water/particle system. Similarly, oxidation of anaerobic sediments increases the availability of certain metals (DiToro *et al.* 1991). Because the availability of contaminants may be a function of the degree of manipulation, this manual recommends that treatment of the sediment prior to testing be as consistent as possible.

3.7.1. Collection Methods

Sediment collections have been made with grab and dredge sampling devices and core samplers. The advantages and disadvantages of the various collection methods have been previously reported (Environment Canada 1994; U.S. EPA 1982ab). All sampling methods disturb the sediment integrity to a degree. For purposes of sediment toxicity evaluations, it is important to obtain sediments with as little disruption as possible. For this reason, core sampling is preferred above other methods. Choosing the most appropriate sediment sampler for a study will depend on the sediment's characteristics, the sampling efficiency required, and the study objectives (U.S. EPA 1982ab; Downing 1984; Plumb 1981). Grab samplers can penetrate sediments to depths of 10 to 50 cm. Dredge samplers collect to a depth of 10 cm and severely disrupt sediment integrity. Core samplers collect up to one or two m when collected by hand or gravity. Vibratory or piston corers, however, can reach penetration depths of up to 10 m. Core penetration depth, normally, is limited to 10 core diameters in sandy substrates and 20 diameters in predominately clay sediments.

Common problems with grab and dredge samplers vary, but include shallow depth of penetration and presence of a shock wave that results in loss of the fine surface sediments. A grab sampler usable in rough water which quantitatively samples the top 1 cm of sediment and retains fine materials has been described by Murray and Murray (1987). Other grab samplers that quantitatively sample surface sediments have been described by Grizzle and Stegner (1985). The depth profile of the sample may be lost in the removal of the sample from the sampler. Some grab samplers promote the loss of not only fine sediments, but also water soluble compounds and volatile organic compounds present in the sediment. Dredge samplers severely disrupt sediment integrity and are poor samplers of fine surficial sediments.

Studies of macroinvertebrate sampling efficiency with various grab samplers have provided useful information for sampling in sediment toxicity and sediment quality evaluations. These data provide information that indicate sampler efficiency at retaining surficial sediment layers. The modified van Veen is commonly used in coastal sampling (U.S. EPA 1991d), and one of these modifications is the sampler of choice for U.S. EPA's EMAP program. The Ekman grab is a commonly used sampler for benthic investigations (Grizzle and Stegner 1985). The Ekman's efficiency is limited to less compacted, fine-grained sediments. Blomqvist (1990) reviewed the various Ekman modifications and their associated problems and concluded that the Ekman grab could be reliably used. In more resistant sediments the Petersen, PONAR, and Smith-McIntyre grabs are used most often (Downing 1984). Based on studies of benthic macroinvertebrate populations, the sediment corers are the most accurate samplers, followed by the Ekman grab, in most cases (Downing 1984). For compacted sediments, the PONAR grab was the most accurate and the Petersen the least (Downing 1984). A comparison of sampler precision indicated the van Veen sampler to be the least precise; the most precise were the corers and Ekman grab (Downing 1984).

Many of the problems associated with grab and dredge samplers are largely overcome with the corers; the most commonly used is the Kajik-Brinkhurst corer. The best corers for most sediment studies are hand-held PTF plastic, high density polyethylene, glass corers (liners), or large box-corers. The corers can maintain the integrity of the sediment surface while collecting sediment at sufficient depths. Furthermore, the box core can be sub-cored or sectioned at specific depth intervals, as required by the study. The box corer, unfortunately, is large and cumbersome; thus, it is difficult to use. Freefall or gravity corers tend to cause compaction, disrupting the vertical gradients in the sediment. Compaction is reduced using the piston corer. Other coring devices which have been successfully used include the percussion corer (Gilbert and Glew 1985) and vibratory corers (Fuller and Meisburger 1982; Imperato 1987; Lanesky *et al.* 1979).

Core samplers have several limitations. Most corers do not work well in sandy sediments; grab samplers or diver-collected material remain the only current alternatives. In general, corers collect less sediment than do grab samplers. Small corers tend to increase bow waves (that is, disturbance of surface sediments) and compaction, thus altering the vertical profile at the sediment surface. As shown by Rutledge and Fleeger (1988) and others, care must be taken in subsampling from core samples, since surface sediments might be disrupted even in hand-held core collection. They recommend subsampling *in situ* or homogenizing core sections before subsampling. For additional information of various core types see (U.S. EPA 1982a).

For studies of sediment toxicity, pore waters, microbiological processes, or chemical fate, core sampling should be used to best maintain the complex integrity of the sediment. When obtaining cores from shallow waters, one must ensure that the vessel does not disturb the sediments before sampling (Sly 1969). If core sampling is not possible due to an inability of the core to penetrate the sediment (*e.g.*, highly compacted sediment), retain the sample (*e.g.*, primarily sand composition), or if large sediment volumes are needed, then grab samplers which reduce the loss of fine grained surficial sediments should be used.

Subsampling, compositing, or homogenization of sediment samples is often necessary and the optimal methods will depend on the study objectives. Important considerations include: sediment integrity and depth profile; potential changes in chemical speciation via oxidation and reduction or other chemical interactions; chemical equilibrium disruption resulting in volatilization, sorption, or desorption; changes in biological activity; completeness of mixing; and chemical characteristics of the sampling container. In most studies of sediment toxicity, it is advantageous to subsample the inner area of the sampler, since this area is most likely to have maintained its integrity and depth profile and not be contaminated by the sampler. Subsamples from the depositional layer of concern should be collected with a nonreactive sampling tool, such as a PTF-lined calibration scoop (U.S. EPA 1986).

For some studies it is advantageous or necessary to composite or mix multiple sediment samples (U.S. EPA 1986). An advantage of composited samples is they reduce the likelihood of missing a "hot spot" due to site heterogeneity. However, the toxicity of "hot spot" samples will be reduced when diluted with cleaner samples. Compositing will result in the loss of information on spatial variability at the site. This loss of information is the most critical issue in the boundary areas of a contaminated site.

Subsamples are collected with a nonreactive sampling scoop and placed in a nonreactive bowl or pan. The composite sample should be mixed until texture and color appear uniform. When collecting sediment samples, it is important to clean the sampling device, scoop, spatula, and mixing bowls between sample sites. The cleaning procedure can follow NOAA

(1987): 1) soap and water wash, 2) distilled water rinse, 3) methanol or acetone rinse, and 4) site water rinse. Waste solvents should be collected in labeled hazardous waste containers.

Sediments should be transported whole, in either plastic, polyethylene (Alden and Butt 1987; Clark *et al.* 1986, 1987), or glass (Jafvert and Wolfe 1987; Wolfe *et al.* 1986) containers under refrigeration or on ice (Jafvert and Wolfe 1987; Wolfe *et al.* 1986; Reichert *et al.* 1985; Giesy *et al.* 1988; Malueg *et al.* 1983; 1984ab; Rubinstein *et al.* 1983). Transport time should be minimized.

Collection, transport, storage, and test chamber material composition should be chosen based on a consideration of sorption effects, sample composition, and contact time. For example, in sediments where organics are of concern, brown borosilicate glass containers with polytetrafluoroethylene (PTF) lid liners are optimal, while plastic containers are recommended for metal samples. PTF or high density polyethylene containers are relatively inert and optimal for samples contaminated with multiple chemical types. Additionally, polycarbonate containers have been shown to not sorb metal species. However, all plastics (including PTF) leach elements and should be preconditioned with 7 day washes in 1:1 HCl, HNO_3, and deionized water (Lindstrom and Moody 1977). Additional information on sample containers, preservation, storage times and volume requirements, in regards to chemical analyses, are available in other guidance documents (U.S. EPA 1982ab, 1986, 1987). In many cases, these criteria are applicable to toxicity test chamber requirements.

3.7.2. Storage

Where sediments contain volatile compounds, transport and storage should be in air tight PTF or glass containers with PTF-lined screw caps. Volatile and semi-volatile compounds must be stored at 4°C for a minimal period of time.

Drying, freezing, and cold storage conditions all affect toxicity and bioavailability (Burton and Stemmer 1987; Lee and Jones 1982, Lee and Plumb 1974; Malueg *et al.* 1986; Stemmer *et al.* 1990). Often the storage time of sediments used in toxicity tests were specified ranges from a few days (Swartz *et al.* 1985a) to one year (Clark *et al.* 1986). Storage of sediments after arrival in the laboratory are generally by refrigeration at 4°C (Alden and Butt 1987; Clark *et al.* 1986, 1987; Malueg *et al.* 1983; Swartz *et al.* 1985ab; Silver 1972; Wood *et al.* 1987). Recommended limits for storage of metal-spiked sediments have ranged from two (Burton and Stemmer 1987) to seven days (Swartz *et al.* 1985a; Anderson *et al.* 1987; Plumb 1980). Cd toxicity in sediments is related to acid volatile sulfide (AVS) complexation (Di Toro *et al.* 1991). When anoxic sediments were exposed to air, AVS are rapidly volatilized. If a study objective is to investigate metal toxicity and the sediment environment is anoxic, then exposure to air might affect toxicity and bioaccumulation due to oxidation and precipitation of the metal species or loss of acid volatile sulfide complexation.

It is generally agreed that sediments to be used for toxicity testing should not be frozen (Malueg *et al.* 1986; Swartz *et al.* 1985a; Swartz 1987; Anderson *et al.* 1987; Stemmer *et al.* 1988). Freezing of sediment cores has been recommended for some metal and organic chemical, and nutrient analyses (U.S. EPA 1991d; Silver 1972; Thomson *et al.* 1980; Rochon and Chevalier 1987). Freezing has been reported to inhibit oxidation of reduced Fe and manganese compounds (Jenne and Zachara 1987). Thomson *et al.* (1980) found that no storage method for sediments preserved initial chemical and physical characteristics of the sediment. Changes were observed at 15 days in sediments stored at 4°C and oxidation was greater than reduction (Thompson *et al.* 1980). If sediments are to be frozen for chemical analyses, it should be a sample split from those used for toxicity testing which are kept at 4°C.

In summary, it is recommended that sediments for toxicity tests and chemical analyses be refrigerated or placed on ice in polyethylene containers during transport. If, in addition, samples are to be used for chemical analyses, then the appropriate container and holding time should be used. The storage conditions should be refrigeration at 4°C and under anoxic conditions if appropriate (Env. Canada 1994, U.S. EPA 1986, 1987; Andersen and Helder 1987). It has been shown that some contaminated sediments can be stored at 4°C for up to 12 months without significant alterations in toxicity (Tatem 1988). Limits to storage time before testing, therefore, appear to be a function of both sediment and contaminant characteristics. Unless there are previous data to indicate the study site sediments can be stored without affecting toxicity, storage time should be limited to two weeks at 4°C.

3.7.3. Manipulations

Manipulation of sediments is often required to yield consistent material for toxicity testing and laboratory experiments. The manipulations reviewed in this section are: (1) mixing; (2) spiking; (3) dilutions for concentration-effect determination; and (4) elutriates.

Mixing: Mixing of sediments is conducted to produce a homogeneous sample which is uniform in color, texture and moisture, and which yields precise results in replicate determinations of toxicity. For field-collected sediments, the sediment quality will be influenced by the depth of sampling, depth of biological activity, contaminant solubility and partitioning characteristics, and depth of the contaminant concentration peak which is dependent on historical contamination and sedimentation rates for the study site. As a result, mixing of various layers of sediments might result in either dilution or enhancement of concentrations. Hand mixing can be accomplished by blending with a spatula (Clark *et al.* 1987; Malueg *et al.* 1986; Burton *et al.* 1989; Pastorok and Becker 1990; Ingersoll and Nelson 1990; Johns *et al.* 1991), rolling the sediment out flat on a sheet of plastic or pre-combusted foil and tumbling by raising each corner of the sheet in succession or by coning and quartering (Mudroch and MacKnight 1991; Landrum *et al.* 1992). A variety of mechanical mixers such as a hand-held drill equipped with a polypropylene or teflon stirrer (*e.g.*, Stemmer *et al.* 1990; Ditsworth *et al.* 1990), a rolling mill (Ditsworth *et al.* 1990; Swartz *et al.* 1990; DeWitt *et al.* 1992), or gyro-rotary and Eberbach shakers (Stemmer *et al.* 1990) have also been used. Mixing time for sediments which vary in color, texture, moisture, and layering will vary but will generally be in the range of one to several minutes (Ditsworth *et al.* 1990; Sasson-Brickson and Burton 1991). Mechanical mixing may alter particle size distribution. Therefore it is recommended that particle size be determined prior to and following the mixing process in order to monitor potential changes in grain size due to the mixing process. Regardless of the mixing method, the efficiency of mixing must also be demonstrated by determining coefficients of variation (Zar 1984) for chemical analyses from replicated samples.

Spiking: Whole sediments may be spiked with specific chemicals in order to determine the effects of single toxicants or mixtures of toxicants on biota (Clark *et al.* 1987; Cairns *et al.* 1984; Muir *et al.* 1982; APHA 1985; Landrum *et al.* 1992; Schuytema *et al.* 1984; Keilty *et al.* 1988ab; Landrum and Faust 1991). The primary method used to spike sediments with contaminants involve wet-spiking techniques. Wet-spiking techniques are currently the most acceptable for the preparation of a spiked sediment, and several techniques have been utilized that are dependent upon the chemical used in spiking (Cairns *et al.* 1984; Landrum *et al.* 1992;

Ditworth *et al.* 1990; Schuytema *et al.* 1984; Francis *et al.* 1984; Landrum and Faust 1981; Birge *et al.* 1987; Suedel *et al.* 1993). Wet-spiking methodologies differ mainly in the amount of water present in the mixture during spiking, the solvent used to apply the toxicant, and the method of mixing. In many cases, the compound is either coated on the walls of the mixing container and an aqueous slurry (sediment and water in various proportions) added, or the carrier-containing mixture is added directly to the slurry. When the sediment-to-water ratio is adjusted for optimal mixing, sediments that are too dense to mix by slurrying in water have been successfully mixed using a rolling mill (Ditsworth *et al.* 1990; Swartz *et al.* 1990; DeWitt *et al.* 1992). In addition to the rolling mill technique, thorough mixing of spiked sediments has been accomplished using Eberbach and gyro-rotary shakers (Stemmer *et al.* 1990). A chemical can also be added to the water overlying the sediment and allowed to sorb with no mixing (Silver 1972; Tsushimoto *et al.* 1982; Lay *et al.* 1984; Stephenson and Kane 1984; O'Neill *et al.* 1985; Crossland and Wolff 1985; Pritchard *et al.* 1986; Gerould and Gloss 1986). Regardless of the technique used for spiking, care should be taken to ensure complete and homogeneous mixing. In addition, chemical analyses should be conducted to ensure that spiking is uniform in the mixed material. Mixing time following spiking should be limited to a few minutes or hours and temperatures kept to a minimum (*e.g.*, 4°C) due to rapid physicochemical and microbiological alterations which may occur in the sediment that in turn may alter bioavailability and toxicity. Mixing time might be extended for recalcitrant organics and some metals (*e.g.*, Cd and Cu) without adverse effects.

3.8. Cost Effectiveness of Metal Analyses of Sediment

3.8.1. Availability and Cost of Commercial Testing

The North American survey which was conducted revealed that very few labs were conducting selective extractions of sediments, but those who did were following protocols similar to Tessier's sequential extraction protocols. While several stated they could do the tests if requested, experience was limited. Cost estimates were based on effort involved and would be relatively inexpensive, as with routine acid digestions of sediments. All surveyed indicated that total metal analyses were commonly conducted, at varying levels of sensitivity. A limited number of laboratories have conducted the AVS/SEM protocol; however, a few good laboratories with experience do exist. These analyses are approximately double ($60-75, US) the cost of routine metal analyses, which are relatively inexpensive ($15 to $50 US, depending on the method and metal; Hg is more expensive).

3.8.2. Data Interpretation

Chemistry data is best interpreted in an integrated, weight-of-evidence approach. As discussed above, when gross contamination exists, chemical data alone is often adequate to establish cause and harm. However, in most situations chemistry should be combined with habitat, biological and toxicity testing. The use of sediment quality guidelines, such as the ERM/ERL or PEL/TELs show promise for routine mining applications. However, given that sediments in mining environments may have metals which are largely present in the biologically unavailable, residual phases, this may not be the case. For this reason, pore water chemistry may be a superior approach and further evaluation of the AVS/SEM approach is needed. Habitat stress is also a significant issue to consider in some mining environments and may show a covariance with metal concentrations.

Conclusions and Recommendations

Conclusions

1. Pore water toxicity testing provides a useful supplement to whole sediment testing.
2. Pore water metal concentrations may be the best indicators of bioavailability. Levels which exceed water quality criteria should be considered harmful.
3. Pore water toxicity testing must be done using carefully controlled collection, extraction, and testing conditions to ensure reliable results.
4. Pore water toxicity testing should only be conducted if adequate quality assurance/quality control (QA/QC) guidelines are followed, which address: 1) appropriate sediment collection methods; 2) appropriate pore water isolation methods; and 3) appropriate toxicity test methods.
5. *In situ* peeper collection of pore waters is the most accurate method, reducing sampling artifacts for chemical analysis and toxicity tests which can be conducted with small sample volumes (single concentration or serial dilutions).
6. *In situ* sample collection and/or testing is preferable to laboratory extraction and/or testing.
7. Reduce sample volume needs by testing only undiluted, single concentration samples in bioassays.
8. When logistical constraints prevent *in situ* sampling, sediments should be collected using the least disruptive method possible. For example, coring is preferred to dredge grab sampling.
9. Efforts must be made to reduce sampling related artifacts, such as oxidation and mixing of vertical gradients.
10. Toxicity testing should commence as soon as possible following extraction.

11. Centrifugation (10,000 x g, 30 min., 4^0C) without filtration is the preferred pore water extraction method if *in situ* collection methods are not feasible. Some sediments may require a double centrifugation to remove small clays and colloidal materials.
12. Appropriate guidelines should be developed for regulatory application of pore water toxicity testing.
13. Few laboratories have experience with pore water toxicity testing; however, qualified laboratories do exist in Canada.
14. Total metal concentrations in sediments are most reliable in situations where gross contamination exists.
15. Easily extractable fractions may be useful on a site specific basis, but are still considered to be in the realm of research.
16. The AVS/SEM approach shows promise with some metals in anaerobic sediments, such as Cd and Ni.
17. Dissolved organic C is likely a primary control factor for Cu availability.
18. An integrated assessment approach is most accurate, combining toxicity testing, biological community characterization, habitat characterization, physicochemical characterization in a tiered testing approach.

Recommendations

1. A field demonstration project at geologically diverse mining sites should be conducted to evaluate utility of pore water toxicity testing.
2. An evaluation program should be developed to field validate the AVS/SEM approach and sediment quality guidelines such as ERLs and PELs for routine application in mining monitoring situations.

5.0. Literature Cited

Adams, D.D. 1991. Sediment pore water sampling. In: A. Mudroch and S.D. MacKnight (eds.), CRC Handbook of Techniques for Aquatic Sediments Sampling, CRC Press, Boca Raton, FL. pp. 171-202.

Adams, W.J., P.S. Ziegenfuss, W.J. Renaudette, and R.G. Mosher. 1986. Comparison of laboratory and field methods for testing the toxicity of chemicals sorbed to sediments. In: T.M. Posten and R. Purdy (eds.), Aquatic Toxicology and Environmental Fate. ASTM STP 921, American Society for Testing and Materials, Philadelphia, PA, pp. 494-513.

Aggett, J. and M.R. Kriegman. 1987. Preservation of As (III) and As (V) in Samples of Sediment Interstitial Water. Analyst, 112: 153-157.

Alden, R.W. and A.J. Butt. 1987. Statistical Classification of the Toxicity and Polynuclear Aromatic Hydrocarbon Contamination of Sediments from a Highly Industrialized Seaport. Environmental Toxicology and Chemistry, 6: 673-684.

Allen, H.E., G. Fu, and B. Deng. 1993. Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. Environ. Toxicol. Chem., 12: 1441-1453.

Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2. A geochemical assessment model for Environmental systems: Version 3.0 Users Manual. USDA, Athens, GA.

American Public Health Association (APHA). 1985. Standard Methods for the Examination of Water and Wastewater, 16th ed, Washington, D.C.

Andrews, D. and J. Fitchko. 1987. Availability of zinc to benthic dwelling organisms from sediment fractions. Ontario Ministry of Environment Technology Transfer. Toronto, Ontario Ministry of Environment, Dorset, Canada.

Ankley, G.T., K. Liber, D.J. Call, T.P. Markee, T.J. Canfield, and C.G. Ingersoll. 1996a. A field investigation of the relationship between zinc and acid volatile sulfide concentrations in freshwater sediments. Journal of Aquatic Health, 5: 255-264.

Ankley, G.T., D.M. Di Toro, D.J. Hansen, and W.J. Berry. 1996b. Technical basis and proposal for deriving sediment quality criteria for metals. Environmental Toxicology & Chemistry, 15: 2056-2066

Ankley, G.T., R.A. Hoke, D.A. Benoit, E.N. Leonard, C.W. West, G.L. Phipps, V.R. Mattson, and L.A. Anderson. 1993. Development and evaluation of test methods for benthic invertebrates and sediments: Effects of flow rate and feeding on water quality and exposure conditions. Arch. Environ. Contam. Toxicol., 25: 12-19.

Ankley, G.T., A. Katko, and J.W. Arthur. 1990. Identification of ammonia as a major sediment-associated toxicant in the lower Fox River and Green Bay, Wisconsin. Environ. Toxicol. Chem., 9: 313-322.

Ankley, G.T., M.K. Schubauer-Berigan, and J.R. Dierkes. 1991. Predicting the toxicity of bulk sediments to aquatic organisms with aqueous test fractions: pore water vs. elutriate. Environ. Toxicol. Chem., 10: 1359-1366.

Ankley, G.T. and M.K. Schubauer-Berigan. 1994. Comparison of techniques for the isolation of sediment pore water for toxicity testing. Arch. Environ. Contam. Toxicol., 27: 517-512.

Ankley G.T., D.E. Tillitt, J.W. Gooch, and J.P. Giesy. 1989. Hepatic enzyme systems as biochemical indications of the effects of contaminates on reproduction of Chinook Salmon *Oncorhyncitus tshawytscha*. Comparative Pharmacology & Toxicology, 94: 235-242.

Apte, S.C., G. Batley, P. Ford, L. Koehnken, and P. Teasdale. 1997. Copper cycling in Macquarie Harbour, Tasmania. Proceedings from 22nd Annual Minerals Council of Australia Environmental Workshop, pp. 362-372.

American Society of Testing and Materials (ASTM). 1994. E. 1367-92 Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods, pp. 1161-1186. *In*: 1994 Annual Book of ASTM Standards, Vol. 11.04, Section 11, Philadelphia, PA.

ASTM. 1995. E. 1391-94 Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing, pp. 479-499. *In*: ASTM Standards on Envionmental Sampling, Philadelphia, PA.

Barnes, R.O. 1973. An *in situ* interslital water sampler for use in unconsolidated sediments. Deep-Sea Research, 20: 1125-1128.

Bascombe, A.D., J. Ellis, D. Revitt, and R. Shutes. 1990. The develoment of ecotoxological criteria in urban catchments. Water Science Technology, 22: 173-179.

Belzile, N., R.R. DeVitre, and A. Tessier. 1989. *In situ* collection of diagenetic iron and manganese oxyhydroxides from natural sediments. Nature, 340: 376-377.

Bendell-Young, L. and H. Harvey. 1992. The relative importance of Mn and Fe oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochimica et Cosmochimica Acta, 56: 1175-1186.

Bender, M., W. Martin, J. Hess, F. Sayles, L. Ball, and C. Lambert. 1987. A Whole-Core Squeezer for Interfacial Pore-Water Sampling, Limnology & Oceanography, 32: 1214-1225.

Benjamin, M.M. and J.O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous Iron oxyhyroxide. J. Colloid Interface Sci., 79: 209-221.

Benson, W.H. and R.T. Di Guilio. 1992. Biomarkers in hazard assessments of contaminated sediments. pp. 241-266 in G.A. Burton, Jr. (ed.) Sediment Toxicity Assessment, CRC/Lewis Publishers, Boca Raton, FL.

Besser, J.M., C.G. Ingersoll, and J.P. Giesy. 1996. Effects of Spatial and Temporal Variation of Acid-Volatile Sulfide on the Bioavailability of Copper and Zinc in Freshwater Sediments. Environmental Toxicology and Chemistry, 15: 286-293.

Berner, R.A. 1980. Early diagenesis: A theoretical approach. Princeton University Press, Princeton.

Berry, W.J., D.J. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin, and W.S. Boothman. 1996. Predicting The Toxicity of Metal-Spiked Laboratory Sediments Using Acid-Volatile Sulfide And Interstitial Water Normalizations. Environmental Toxicology and Chemistry, 15: 2067-2079

Birge, W.J., J. Black, S. Westerman, and P. Francis. 1987. Toxicity of Sediment-Associated Metals to Freshwater Organisms: Biomonitoring Procedures in Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems, Pergamon Press, New York, pp. 199-218.

Bischoff, J.L., R.E. Greer, and A.0. Luistro. 1970. Composition of interstitial waters of marine sediments: temperature of squeezing effect. Science, 167: 1245-1246.

Blomqvist, S. 1990. Sampling performance of Ekman grabs – *in situ* observations and design improvements. Hydrobiologia, 206: 245-254.

Bollinger, R., H. Brandl, P. Hohener, K.W. Hanselmann, and R. Bachofen. 1992. Squeeze-water analysis for the determination of microbial metabolites in lake sediments: Comparison of methods. Limnol. Oceanogr., 37: 448-455.

Bottomley, E.Z. and I.L. Bayly. 1984. A sediment porewater sampler used in root zone studies of the submerged macrophyte, *Myriophyllum spicaum*. Limnology & Oceanography, 29: 671-673.

Boulegue, J., C.J. Lord, and T.M. Church. 1982. Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great March, Delaware. Geochim. Cosmochim. Acta., 46: 453-464.

Brannon, J.M., R. Engler, J. Rose, P. Hunt, and I. Smith. 1976. Selective Analytical Partitioning of Sediments to Evaluate Potential Mobility of Chemical Constituents During Dredging and Disposal Operations. Tech. Rep. D-76-7. U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS.

Bray, J.T., O.P. Bricker, and B.N. Troup. 1973. Phosphate in interstitial waters of anoxic sediments: Oxidation effects during sampling procedure. Science, 180: 1362-1364.

Brendel, P.J. and G.W. Luther, III. 1995. Devolpment Of A Gold Amalgam Voltammatric Microelctrode For The Determination Of Dissolved Fe, Mn, O_2, And S (-11) in Porewaters Of Marine And Freshwater Sediments. Environ. Sci. Technol., 29: 751-761.

Brinkman, A.G., W. van Raaphorst, and L. Lijklema. 1982. *In situ* sampling of interstitial water from lake sediments. Hydrobiologia, 92: 659-663.

Brouwer, H. and T. Murphy. 1995. Volatile Sulfides and Their Toxicity in Freshwater Sediments, Environmental Toxicology & Chemistry, 14: 203-208.

Brownawell, B.J. and J.W. Farrington. 1986. Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment. Geochim Cosmochim. Acta, 50: 157-169.

Brumbaugh, W.G., C.G. Ingersoll, N.E. Kemble, T.W. May, and J.L. Zajicek. 1994. Chemical Characterization of Sediments and Pore Water from the Upper Clark River and Milltown Resevoir, Montana. Environmental Toxicology and Chemistry, 13: 1971-1983.

Bryan, G.W. 1985. Bioavalability and effects of heavy metals in marine deposits, pp. 41-79. B. Ketchum *et al.* [eds.], Wastes in the Ocean. V. 6. Wiley.

Buddensiek, V., H. Engel, S. Fleischauer-Rössing, S. Olbrich, and K. Wächtler. 1990. Studies on the chemistry of interstitial water taken from defined horizons in the fine sediments of bivalve habitats in several northern German lowland waters: I. Sampling Techniques. Arch. Hydrobiol., 119: 55-64.

Bufflap, S.E. and H.E. Allen. 1995a. Sediment pore water collection methods for trace metal analysis: a review. Water Res., 29: 165-177.

Bufflap, S.E. and H.E. Allen. 1995b. Comparison of pore water sampling techniques for trace metals. Water Res., 29: 2051-2054.

Burgess, R.M., K.A. Schweitzer, R.A. McKinney, and D.K. Phelps. 1993. Environ. Toxicol. Chem., 12: 127-138.

Burton, G.A., Jr., B.L. Stemmer, K.L. Winks, P.E. Ross, and L.C. Burnett. 1989. A multitrophic level evaluation of sediment toxicity in Waukegan and Indiana Harbors. Env. Toxicol Chem., 8: 1057-1066.

Burton, G.A., Jr. 1992. Sediment collection and processing: factors affecting realism, In: G.A. Burton, Jr. (ed.) Sediment Toxicity Assessment. Lewis Publishers. Boca Raton, FL. pp. 37-66.

Burton, G.A., Jr. 1991. Assessing the toxicity of freshwater sediments. Environ. Toxicol. Chem., 10: 1585-1627.

Burton, G.A., Jr. and C. Rowland. 1995. The Upper Illinois Waterway Study Summary Report - Sediment Contamination Assessment. Commonwealth Edison Co., Chicago, IL.

Burton, G.A., Jr. and B.L. Stemmer. 1987. Factors affecting effluent and sediment toxicity using cladoceran, algae, and microbial indicator assays, In: Abstr. Annu. Meet. Soc. Environ. Toxicol, Pensacola, FL.

Burton, G.A., Jr., C. Ingersoll, L. Burnett, M. Henery, M. Hinman, S. Klaine, P. Landrum, P. Ross, and M. Tuchman. 1996. A comparison of sediment toxicity test methods at three Great Lake Areas of concern. J. Great Lakes Res., 22: 495-511.

Cai, W.J. and C.E. Reimers. 1993. The development of H^+ and CO_3 microelectrodes for studying the carbonate chemistry of pore waters near the sediment-water interface, Limnol. Oceanogr., 38: 1762-1773.

Cairns, M. A., V. Nebeker, J.H. Gakstatter, W.L. Griffis. 1984. Toxicity of Copper-Spiked Sediments to Freshwater Invertebrates. Environmental Toxicology & Chemistry, 3: 435-445.

Campbell, P.G.C. 1995. Interactions between Trace Metals and Aquatic Organisms: A Critique of the Free-ion Activity Model. pp. 45-102 in A. Tessier and D. Turner (eds.). Metal Speciation and Bioavailability in Aquatic Systems. Shulevey, NY.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, A.A. Crowder, W.K. Fletcher, B. Imber, S.N. Luoma, P.M. Stokes, and M. Winfrey. 1988. Biologically Available Metals in Sediments. National Research Council Canada. NRCC No. 27694. Ottawa, Canada. 298 pp.

Campbell, P.G.C. and A. Tessier. 1994. Geochemistry and bioavailability of trace metals in Sediments, In: A. Boudon and F. Robeyre (eds.) Aquatic Ecotoxicity: Fundamental Concepts and Methodologies, Vol. 1, pp. 125-148. CRC Press, Boca Raton, FL.

Campbell, P.G.C. and A. Tessier. 1984. Paleolimnological approaches to the study of acid deposition: metal partitioning in lacustrine sediments. In Proceedings S.A. Norton (Ed.), Rockport, Maine, pp. 234-274.

Canfield, T.J., N.E. Kemble, W.G. Brumbaugh, F.J. Dwyer, C.G. Ingersoll, and J.F. Fairchild. 1994. Chemical Characterization of Sediments and Pore Water from the Upper Clark Fork River and Milltown Reservoir, Montana. Environmental Toxicology & Chemistry, 13: 1999-2012.

Carignan, R. 1984. Interstitial water sampling by dialysis: methodological notes. Limnol. Oceanogr., 29: 667-670.

Carignan, R. and D.R.S. Lean. 1991. Regeneration of dissolved substances in a seasonally anoxic lake: The relative importance of processes occurring in the water column and in the sediments. Limnol. Oceanogr., 36: 683-707.

Carignan, R., F. Rapin, and A. Tessier. 1985. Sediment Porewater Sampling for Metal Analysis: A Comparison of Techniques, Geochim. Cosmochim. Acta, 49: 2493-2497.

Carignan, R., S. St-Pierre and R. Gachter. 1994. Use of diffusion samplers in oligotrophic lake sediments: effects of free oxygen in sampler material. Limnol. Oceanogr., 39: 468-474.

Carlson, A.R., G.L. Phipps, V.R. Mattson, P.A. Kosian, and A.M. Colter. 1991. The role of acid volatile sulfide in determining Cd bioavaliability and toxicity in freshwater sediments. Environmental Toxicology & Chemistry, 10: 1309-1319.

Carlson-Ekvall, C.E.A. and G.M. Morrison. 1992. Fractionation and Toxicity of Metals in Sewage Sludge. Env. Technology, 13: 751-759.

Carlson-Ekvall, C.E.A. and G.M. Morrison. 1995. Contact toxicity of metals in sewage sludge: evaluation of alternatives to NaCl in the Microtox® assay. Environ. Toxicol. Chem., 14: 17-22.

Carlton, R.G. and M.J. Klug. 1990. Spatial and temporal variation in microbial processes in aquatic sediments: implications for the nutrient status of lakes. In: R. Baudo, J. Giesy, and H. Muntau (eds.) Sediments: Chemistry and Toxicity of In-Place Pollutants. pp. 107-130. Lewis Pulbishers, Boca Raton, FL.

Carlton, R.G. and R.G. Wetzel. 1985. A box corer for studying metabolism of epipelic microorganisms in sediment under *in situ* conditions. Limnol. Oceanogr., 30: 422-426.

Carr, R.A. and P.E. Wilkniss. 1973. Short-term Storage of Natural Waters. Environ. Sci. Technol., 7: 62-63.

Carr, R. S., J.W. Williams, and C.T.B. Fragata. 1989. Development and Evaluation of a Novel Marine Sediment Pore Water Toxicity Test with the Polychaete *Dinophilus gyrociliatus* Environmental Toxicology & Chemistry, 8: 533-543.

Carvalho, Paulo Se'rgio Martins de, Eliete Zanardi, Sandra Vale'ria Buratini, Marta Conde' Lamparell and Magali Coimbra Martins. 1998. Oxidizing Effect On Metal Remobilization And *Daphnia similis* Toxicity From A Brazilian Reservoir Sediment Suspension, Water Research, 32: 193-199.

Casas, A.M. and E.A. Crecelius. 1994. Hazard Assessment: Relationship Between Acid Volatile Sulfide and the Toxicity of Zinc, Lead and Copper in Marine Sediments. Environmental Toxicology & Chemistry, 13: 529-536.

Chapman, P.M. 1996. Hazardous identification, classification and risk assessment for metals and metal compounds in the aquatic environment. International Council on Metals and the Environment, Ottawa, Ontario. 31 pp.

Chapman, P.M. and R. Fink. 1984. Effects of Puget Sound sediments and their elutriates on the life cycle of *Capitella capitata*. Bull. Environ. Contam. Toxicol., 33: 451-459.

Chapman, P.M., F. Wang, C. Janssen, G. Persoone, and H.E. Allen. 1997. Ecotoxicology of Metals in Aquatic Sediments: Binding and Release, Bioavailability, Hazard, Risk, and Remediation, Draft Report for Kennecott Mines.

Chapman, P.M. 1997. Is bioaccumulation useful for predicting impacts? Mar. Pollut. Bull., 34: 282-283.

Chappie, D.J. and G.A. Burton, Jr. 1997. Optimization Of *In Situ* Bioassays With *Hyalella azteca* and *Chironomus tentans*. Environ. Toxicol. Chem., 16: 559-564.

Chen, W. and G.M. Morrison. 1994. Inhibition of bacterial enzyme activity and luminescence by arburive sediments. Sci. Total. Env., 146/147: 141-147.

Chin, Y. and P.M. Gschwend. 1991. The abundance, distribution, and configuration of porewater organic colloids in recent sediment. Geochim. Cosmochim. Acta, 55: 1309-1317.

Clark, J.R., J.M. Patrick, J.C. Moore, and J. Forester. 1986. Accumulation of Sediment-Bound PCBs by Fiddler Crabs, Bulletin of Environmental Contamination & Toxicology, 36: 571-578.

Clark, J. R., J.M. Patrick, J.C. Moore, and E.M. Lores. 1987. Waterborn and Sediment-Source Toxicities of Six Organic Chemicals to Grass Shrimp (*Palaemonetes pugio* and Amphioxus (*Branchiostoma caribaeum*), Archives of Environmental Contamination & Toxicology, 16: 401-407.

Cooper, D.C. and J.W. Morse. 1998. Extractability of Metal Sulfide Minerals in Acidic Solutions: Applications to Environmental Studies of Trace Metal Contamination within Anoxic Sediments. Environmental Science & Technology, 32: 1076-1078.

Couillard, Y., P.G. C. Campbell, and A. Tessier. 1993. Response of Metallothionein Concentrations in a Freshwater Bivalve (*Anodonta grandis)* Along an Environmental Cd Gradient. Limnol. Oceanogr., 38: 299-313.

Cowan, C.E., E.A. Jenne, and R.R. Kinnison. 1986. Microbiology for determining the relationship between toxicity and the aqueous speciation of a metal. In: T.M. Poston and R. Purdy (eds.) Aquatic Toxicology and Environmental Fate, 9: 463-478. ASTM Spec. Tech. Publ. 921, Amer. Soc. Testing & Materials, Philadelphia, PA.

Crecelius, E. A., E.A. Jenne, and J.S. Anthony. 1987. Sediment Quality Criteria for Metals: Optimization of Extraction Methods for Determining the Quantity of Sorbents and Adsorbed Metals in Sediments, Battelle Report to U.S. EPA, Criteria and Standards Division, Washington, DC.

Crosby, S.A., D.R. Glasson, A.H. Cuttler, I. Butler, D.R. Turner, M. Whitfield, and G.E. Millward. 1983. Surface areas and porosities of Fe(III)- and Fe(II)-derived oxyhydroxides. Enviro. Sci. Technol., 17: 709-713.

Crossland, N.0. and C.J.M. Wolff. 1985. Fate and Biological Effects of Pentachlorophenol in Outdoor Ponds, Environmental Toxicology & Chemistry, 4: 73-86.

Daniels, S.A., M. Munawar, and C.I. Mayfield. 1989. An improved elutriation technique for the bioassessment of sediment contaminants. Hydrobiol., 188/189: 619-631.

Davis, J.A. 1984. Complexation of trace metals by adsorbed natural organic matter. Geochim. Cosmochim. Acta, 48: 679-691.

Davies-Colley, R.J., P. Nelson, and K.J. Williamson. 1984. CopPer and cadmium uptake by estuarine sediment phases. Environ. Sci. Technol., 18: 491-499.

Davison, W., G.W. Grime, J.A.W. Morgan, and K. Clarke. 1991. Distribution of dissolved iron in sedimentary pore waters at submillimeter resolution. Nature, 352: 323-325.

Davison, W. and H. Zhang. 1994. *In situ* speciation measurements of trace metal components in natural waters using thin-film gels. Nature, 367: 546-548.

Deaver, E. and J.H. Rodgers 1996. Measuring bioavailable copper using anodic stripping voltammetry. Environ. Toxicol. Chem., 15: 1925-1930.

Decaprio 1997. Biomarkers: coming of age for environmental health and risk assessment. Environ. Sci. Technol., 31: 1837-1848.

De Vitre, R., N. Belzile, and A. Tessier. 1991. Speciation and Adsorption of Arsenic On Diagenetic Fe Oxyhydroxides. Limnology and Oceanography, 36: 1480-1485

DeWitt, T.H., R.C. Swartz, and J.0. Lamberson. 1989. Measuring the acute toxicity of estuarine sediments. Environ. Toxicol. Chem., 8: 1035-1048.

DeWitt, T.H., R.J. Ozrethich, R.C. Swartz, J.0. Lamberson, D.W. Schults, G.R. Ditsworth, J.K.P. Jones., L. Hoselton, and L.M. Smith. 1992. The influence of organic matter quality on the toxicity and partitioning of the sediment-associated fluoranthene. Environ. Toxicol Chem., 16: 401-407.

De Witt, T.H., R.C. Swartz, D.J. Hansen, D. McGovern, and W.J. Berry. 1996. Bioavailability and Chronic Toxicity of Cd in Sediments to the Estuarine Amphipod *Leptocheirus plumulosus.* Environmental Toxicology and Chemistry, 15: 2095-2101.

Di Toro, D.M., J.D. Mahoney, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr, and M.S. Redmond. 1990. Toxicity of cadmium sediments: the role of acid volatile sulphide. Environ. Toxicol. Chem., 9: 1487-1502.

Di Toro, D.M., C.J. Zarba, D.J. Hansen, W.J. Berry, R.W. Swartz, C.E. Cowna, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem., 10: 1541-1583.

Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, A.R. Carlson, and G.T. Ankley. 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. Environ. Sci. Technol., 26: 96-101.

Di Toro, D.M., J.D. Mahony, and A.M. Gonzalez. 1996a. Particle Oxidation Model of Synthetic FeS and Sediment Acid-Volatile Sulfide. Environ. Toxicol. & Chem., 15: 2156-2167.

Di Toro, D.M., J.D. Mahony, D.J. Hansen, and W.J. Berry. 1996b. Partitioning of Metals to Sediment Organic Carbon. Environmental Toxicology and Chemistry, 15: 2187-2197.

Ditsworth, G.R., D.W. Schults, and J.K.P. Jones. 1990. Preparation of benthic substrates for sediment toxicity testing. Environ. Toxicol. Chem. 9: 1523-1529.

Downing, J. A., 1984. Sampling the Benthos of Standing Waters, A Manual on Methods for the Assessment of Secondary Productivity in Freshwaters, 2nd Edition, IBP Handbook 12, Blackwell Scientific Publications, Boston, MA, pp. 87-130.

Dzombak, D. and F.M.M. Morel. 1990. Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons, New York, NY, 393 pp.

Edmunds, W.M., and A.H. Bath. 1976. Centrifuge Extraction and Chemical Analysis of Interstitial Waters, Environmental Science & Technology, 10: 467-472.

Emerson, S., L. Jacobs, and B. Tebes. 1983. The Behavior of Trace Metals in Marine Anoxic Waters: Solubilities at the Oxygen-Hydrogen Sulfide Interface: *In*: C. S. Wong, E. Boyle, K. Bruland and J. Burton (eds) Trace Metals in Sea Water. pp. 579-605, Plenum Press New York.

ENSR 1997. 1996 Clark Fork River sediment benthic macroinvertebrate assessment. Draft Report to Atlantic Richfield Cor. , Anaconda, Montana. No. 0480-396-290.

Engler, R.M., J. Brannon, J. Rose, and G. Bigham. 1977. A Practical Selective Extraction Procedure for Sediment Characterization, Chemistry of Marine Sediments, Ann Arbor Sci., Ann Arbor, MI, pp. 163-171.

Environment Canada. 1992a. Fertilization Assay with Echinoids (Sea Urchins and Sand Dollars), EPS 1/RM/27.

Environment Canada. 1992b. Toxicity Testing Using Luminescent Bacteria (*Photobacterium phosphoreum*), EPS1/RM/24.

Environment Canada. 1994. Collection and Preparation of Sediment for Physicochemical Characterization and Biological Testing. EPS 1/RM/29.

Environment Canada. 1996. Canadian Sediment Quality Guidelines For Cadmium. Cd SQGs: Pre-Publication Draft.

Erickson, R.J., D.A. Benoit, V.R. Mattson, A.P. Melson, and E.N. Leonard. 1996. The Effects of Water Chemistry on the Toxicity of Copper to Fathead Minnows, Environ. Toxicol. Chem., 15: 181-193.

Fisher, R. 1991. Sediment Interstitial Water Toxicity Evaluations Using *Daphnia magna*. Thesis, M.Sc. degree. Wright State University, Dayton, OH

Fisher, N.S. 1986. On the Reactivity of Metals for Marine Phytoplankton. Limnol. Oceanogr., 31: 443-449.

Förstner, U. 1995. Non-linear Release of Metals from Aquatic Sediments. *In*: W. Salomons and W.M. Stigliani (eds). Biogeodynamics of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-linear Resposes. pp. 267-307. Springer Verlag, Berlin.

Francis, P.C., W. Birge, and J. Black. 1984. Effects of Cd-Enriched Sediment on Fish and Amphibian Embryo-Larval Stages, Ecotoxicology & Environmental Safety, 8: 378-387.

Frazier, B.E., T.J. Naimo, and M.B. Sandheinrich. 1996. Temporal and Vertical Distribution of Total Ammonium Nitrogen and Unionized Ammonia Nitrogen in Sediment Pore Water from the Upper Mississippi. Environ. Toxicol. Chem., 15: 92-99.

Froelich, P.M., G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartmann, and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta, 43:1075-1090.

Fu, G., H.E. Allen, and Y. Cao. 1992. The importance of humic acids to protein and cadmium binding in sediments. Environ. Toxicol. Chem., 141: 1363-1372.

Fuller, J. A. and E.P. Meisburger. 1982. A Simple, Ship-Based Vibratory Corer, Journal of Sediment Petrology, 52: 642-644.

Gagnon, C., A. Mucci, and E. Pelletier. 1996. Vertical Distribution of Dissolved Sulfide Species Selection and Test Design. J. G. Lakes Res., 15: 539-569.

Gagnon, C. and N.S. Fisher. 1997. Bioavailability of Sediment-Bound Methyl and Inorganic Mercury to a Marine Bivalve, Environmental Science & Technology, 31: 993-998.

Gambrell, R.P., R.A. Khalid, and W.H. Patrick, Jr. 1976. Physicochemical parameters that regulate mobilization and immobilization of toxic heavy metals. Proceedings, Specialty Conference on Dredging and Its Environmental Effects, Mobile, AL, American Society of Civil Engineers, New York, NY, pp. 418-434.

Gerould, S. and S.P. Gloss. 1986. Mayfly-Mediated Sorption of Toxicants into Sediments, Environmental Toxicology & Chemistry, 5: 667-673.

Giesy, J.P., R.L. Graney, J.L. Newsted, C.J. Rosiu, A. Benda, R.G. Kreis, and F.J. Horvath. 1988. Comparison of Three Sediment Bioassay Methods Using Detroit River Sediments, Environmental Toxicology & Chemistry, 7: 483-498.

Giesy, J.P., C.J. Rosiu, R.L. Graney, and M.G. Henry. 1990. Benthic invertebrate bioassays with toxic sediment and pore water. Environ. Toxicol. Chem., 9: 233-248.

Gonzalez, A.M. 1995. A laboratory-formulated sediment incorporating synthetic acid volatile sulfide. Abstr. PH135, p. 310. Annu. Meet. Soc. Environ. Toxicol. Chem., Vancouver, B.C.

Gonzalez, A. M. 1996. A laboratory-formulated sediment incorporating synthetic acid volatile sulfide. Environmental Toxicology and Chemistry, 15: 2209-2220.

Green, A.S., G.T. Chandter, and E.R. Blood. 1993. Aqueous-, pore-water-, and sediment-phase cadmium: Toxicity relationships for a meiobenthic copepod. Environmental Toxicology and Chemistry, 12: 1497-1506.

Grizzle, R.E. and W.E. Stegner. 1985. A new quantitative grab for sampling benthos. Hydrobiologia, 126: 91-95.

Hamoutene, D., M. Romeo, M. Gnassia, and M. Lafaurie. 1996. Cadmium Effects of Oxidative Metabolism in a Marine Seagrass: *Posidonia Oceanica.* Bull. Environ. Contam. Toxicol., 56: 327-334.

Hansen, D.J., J.D. Mahony, W.J. Berry, S.J. Benyi, J.M. Corbin, S.D. Pratt, D.M. Di Torro, and M.B. Abel. 1996a. Chronic Effect of Cadmium in Sediments on Colonization by Benthic Marine Organisms: An Evaluation of the Interstitial Cadmium and Acid-Volatile Sulfide in Biological Availability. Environmental Toxicology and Chemistry, 15: 2126-2137.

Hansen, D.J., W.J. Berry, J.D. Mahony, W.S. Boothman, D.M. Di Toro, D.L. Robson, G.T. Ankley, D. Ma, Q. Yan and C.E. Pesch. 1996b. Predicting the Toxicity of Metal-Contaminated Field Sediments Using Interstitial Concentration of Metals and Acid-Volatile Sulfide Normalizations. Environmental Toxicology and Chemistry, 15: 2080-2094.

Hare, L., P. Campbell, A. Tessier, and N. Belzile. 1989. Gut Sediments in a Burrowing Mayfly (Ephemeroptera, *Hexagenia limbata*): Their Contribution to Animal Trace Element Burdens, Their Removal, and the Efficacy of a Correction for Their Presence. Can. J. Fish. Aquat. Sci., 46: 451-456.

Hare, L., R. Carignan, and M.A. Huerta-Diaz. 1994. A Field Study of Metal Toxicity and Accumulation by Benthic Invertebrates; Implications for the Acid-Volatile Sulfide (AVS) Model, Limnol. Oceanogr., 39: 1653-1668.

Hare, L. 1992. Aquatic insects and trace metals; bioavalability, bioaccumulation, and toxicity. Crit. Rev. Toxicology, 22: 327.

Hare, L. and F. Shooner. 1995. Do Aquatic Insects Avoid Cadmium-Contaminated Sediments? Environmental Toxicology and Chemistry, 14: 1071-1077.

Hare L. and A. Tessier. 1996. Predicting Animal Carbon Concentration in Lakes. Nature, 380: 430-432.

Hare, L., A. Tessier, and L. Warren. Sedimentary Metal Bioaccumulation and Toxicity: Assumptions, Assessment, Research Needs. SETAC News, March 1998. Soc. Environ. Toxicol. Chem., Pensacola, FL.

Hare, L., E. Saouter, P. Campbell, A. Tessier, F. Ribeyre, and A. Boudou. 1991. Dynamics of Cadmium, Lead, and Zinc Exchange between Nymphs of the Burrowing Mayfly *Hexagenia rigida* (Ephemeroptera) and the Environment. Can. J. Fish. Aquat. Sci., 48: 39-47.

Harkey, G.A., P.F.Landrun, and S.J. Klaine. 1994. Comparison of whole sediment, elutriate and pore water exposures for use in assessing sediment associated organic contaminants in bioassays. Environ. Toxicol. Chem., 13: 1315-1329.

Hesslin, R.H., 1976. An In Situ Sampler for Close Interval Pore Water Studies, Limnology & Oceanography, 21: 912-914.

Hill, J.R., P. Mathiessen, and F. Heimbach (eds). 1994. Guidance Document on Sediment Toxicity Tests and Bioassays for Freshwater and Marine Environments. Europe SETAC., Brussels, Belgium.

Hintelmann, H., P.M. Welbourn, and R. Douglas Evans. 1997. Meaurement of Complexation of Methylmercury (II) Compounds by Freshwater Humic Substances Using Equilibrium Dialysis, Environmental Science & Technology, 31: 489-495.

Hooten, R.L. and R. Scott Carr. 1998. Development and Application of a Marine Sediment Pore-water Toxicity Test Using *Ulva fasciata* Zoospores, Environmental Toxicology and Chemistry, 17: 932-940.

Howard, D.E. and R.D. Evans . 1993. Acid-Volatile Sulfide (AVS) In A Seasonally Anoxic Mesotrophic Lake: Seasonal and Spatial Changes In Sediment AVS. Environ. Toxicol. Chem., 12: 1051-1057.

Howes, B.L., J.W.H. Dacey, and S.G. Wakeham. 1985. Effects of Sampling Technique on Measurements of Porewater Constituents in Salt Marsh Sediments, Limnology & Oceanography, 30: 221-227.

Huerta-Diaz, M.A., A. Tessier, and R. Carignan. 1997. Geochemistry of trace metals associated with reduced sulfur in freshwater sediment. Applied Geochemistry. In press.

Huerta-Diaz, M.A., R. Carignan, and A. Tessier. 1993. Measurement of trace metals associated with acid volatile sulfides and pyrite in organic freshwater sediments. Environ. Sci. Technol., 27: 2367-2372.

Huettel, M. and G. Gust. 1992. Impact of Bioroughness on Interfacial Solute Exchange In Permeable Sediments, Marine Ecology Progress Series, 89: 253-267.

Hugget, R.J., P.A. VanVeld, C. Smith, W. Hargin, W. Volgelbein, and B. Weeks. 1992. The effects of contaminated sediment in the Elizabeth River. *In*: G.A. Burton, Jr. (ed.) Sediment Toxicity Assessment. CRC/Lewis Publ. Boca Raton, FL. pp. 403-430.

Hulbert, M.H. and M.P. Brindle. 1975. Effects of Sample Handling on the Composition of Marine Sedimentary Pore Water, Geological Society of America Bulletin, 86: 109-110.

Imperato, D. 1987. A Modification of the Vibracoring Technique for Sandy Sediment, J. Sediment Petrol., 57: 788-789.

Ingersoll, C.G. and M.K. Nelson. 1990. Testing sediment toxicity with *Hyalella azteca* (Amphipoda) and *Chironomus riparius* (Diptera). *In:* W.G. Landis and W.H. van der Schalie (eds.), Aquatic Toxicology and Risk Assessment, Volume 13, ASTM STP 1096. ASTM. Philadelphia, PA., pp. 93-109.

Ingersoll, C.G., W.G. Brumbaugh, F.J. Dwyer, and N.E. Kemble. 1994. Bioaccumulation of Metals by *Hyalella azteca* Exposed to Contaminated Sediments From the Upper Clark Fork River, Montana. Environ. Toxicol. Chem., 13: 2013-2120.

Ingersoll, C.G., G.T.Ankley , R. Baudo, G.A. Burton, W. Lick, S.N. Luoma, D.D. MacDonald, T.B. Reynoldson, K.R. Solomon, R.C. Swartz, and W. Warren-Hicks, 1997. Workgroup summary report on an uncertainty evaluation of measurement endpoints used in sediment ecological risk assessments. *In:* Ingersoll, C.G., T. Dillon, and G.R. Biddinger (eds.). Ecological Risk Assessments of Contaminated Sediments. Proceedings of the 22nd Pellston Workshop, SETAC Special Publication Series, SETAC Press, Pensacola FL. pp. 297-352.

Jafvert, C.T. and N.L. Wolfe. 1987. Degradation of Selected Halogenated Ethanes in Anoxic Sediment-Water Systems, Environ. Toxicol. Chem., 6: 827-837.

Jahnke, R.A. 1988. A simple, reliable, and inexpensive pore-water sampler. Limnol. Oceanogr., 33: 483-487.

Janssen, C.R., M.L. Vangheluwe, and G. Persoone. 1995. A Multi-factorial Study of the Effect of Collection, Storage and Extraction Techniques on the Toxicity of Freshwater Sediments. Abstr. Annu. Meet. Soc. Environ. Toxicol. Chem. p. 264.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Ca, and Zn concentrations in soils and water: The significant role of Hydrous Mn and Fe Oxides, Advanced Chem., 73: 337-387.

Jenne, E.A. 1977. Trace element sorption by sediments and soil-sites and processes, *In:* Symposium on Molybdenum in the Environment, Vol. 2, M. Dekker, Inc., New York, pp. 415-553.

Jenne, E. A. 1987. Sediment Quality Criteria for Metals: II. Review of Methods for Quantitative Determination of Important Adsorbants and Sorbed Metals in Sediments, Battelle Report to U.S. EPA, Criteria and Standards Division, Washington, DC.

Jenne, E.A. and J.M. Zachara. 1987. Factors Influencing the Sorption of Metals, *In*: Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems, Pergamon Press, New York, pp. 83-98.

Johns, D.M., R.A. Pastorak, and T.C. Ginn. 1991. A sublethal sediment toxicity test using juvenile Neanthes sp. (Polychaeta: Nereidae), pp. 280-293. In: M.A. Mayes and M.G. Barron, (eds.) Aquatic Toxicology and Risk Assessment, Vol. 14, ASTM STP 1124. ASTM, Philadelphia, PA. 383 pp.

Jung, K., G. Bitton, and B. Koopman. 1996. Selective Assay for Heavy Metal Toxicity Using A Fluorogenic Substrate, Environmental Toxicology and Chemistry, 15: 711-714.

Kalil, E.K. and M. Goldhaker. 1973. A Sediment Squeezer for Removal of Pore Waters Without Air Contact, Journal of Sediment Petrology, 43: 553-557.

Keilty, T.J., D.S. White, and P.F. Landrum. 1988a. Sublethal Responses to Endrin in Sediment by *Stylodrilius heringianus* (Lumbriculidae) as Measured by a 137Cesium Marker Layer Technique. Aquatic Toxicology, 13: 227-250.

Keilty, T.J., D.S. White, and P.F. Landrum. 1988b. Short-Term Lethality and Sediment Avoidance Assays with Endrin-Contaminated Sediment and Two Oligochaetes from Lake Michigan, Archives of Environmental Contamination & Toxicology, 17: 95-101.

Kemble, N.E., W.G. Brumbaugh, E.L. Brunson, F.J. Dwyer, C.G. Ingersoll, D.P. Monda, and D.F. Woodward. 1994. Toxicity of metal contaminated sediment from the upper Clark Fork River, Montana to aquatic invertebrates and fish in laboratory exposures. Environ. Toxicol. Chem., 13: 1985-1997.

Kemp, P.F. and R.C. Swartz. 1986. Acute toxicity of interstitial and particle-bound cadmium to a marine infaunal amphipod. Mar. Environ. Res., 26: 135-153.

Kersten, M. and U. Förstner. 1987. Cd Associations in Freshwater and Marine Sediment, Cadmium in the Aquatic Environment, John Wiley & Sons, New York, pp. 51-88.

Khalid, R.A., R.P. Gambrell, and W.H. Patrick. 1981. Chemical availability of Cadmium in Mississippi River sediment. J. Env. Qual., 10:523-528.

Kikuchi, E. and Y. Kurihara. 1977. Oikos, 29: 348-356.

Klinkhammer, G.P. 1980. Early Diagenesis in Sediments from the Eastern Equatorial Pacific. II. Pore Water Metal Results. Earth Planet. Sci. Lett., 49: 81-101.

Knezovich, J.P. and F.L. Harrison. 1987. A New Method for Determining the Concentrations of Volatile Organic Compounds in Sediment Interstitial Water, Bull. Environ. Contam. Toxicol., 38: 937-940.

Kriukov, P.A. and F.T. Manheim. 1982. Extraction and investigative techniques for study of interstitial waters of unconsolidated sediments: a review. *In*: K.A. Fanning and F.T. Manheim (eds), The Dynamic Environment of the Ocean Floor. Lexington Books, Washington, D.C., pp. 3-26.

Krom, M.D., P. Davidson, H. Zhang, and W. Davidson. 1994. High-resolution pore-water sampling with a gel sampler. Limnol. Oceanogr., 39: 1967-1972.

Lake, D.L., P. Kirk, and J. Lester. 1984. Fractionation, Characterization, and Speciation of Heavy Metals in Sewage Sludge and Sludge-Amended Soils: A Review, Journal of Environmental Quality, 13: 175-183.

Landrum, P.F., S.R. Nihart, B.J. Eadie, and L.R. Herche. 1987. Reduction in Bioavailability of Organic Contaminants to the Amphipod *Pontoporeia hoyi* by Dissolved Organic Matter of Sediment Interstitial Waters, Environmental Toxicology Chemistry, 6: 11-20.

Landrum, P.F. and W.R. Faust. 1991. Effect of variation in sediment composition on the uptake rate coefficient for selected PCB and PAH cogeners by the amphipod, *Diporeia sp.*, pp. 263-279. *In*: M.A. Mayes and M.g. Barron (eds.) Aquatic toxicology and risk assessment ASTM STP 1124. ASTM, Pa.

Landrum, P.F., B.J. Eadie and W.R. Faust. 1992. Variation in the bioavailability of polycyclic aromatic hydrocarbons to the amphipod *Diporeia (spp.)* with sediment aging. Environ. Toxicol. Chem., 11: 1197-1208.

Laxen, D.P.H. 1983. Trace metal adsorption/copoecipitahomon hydrons ferric oxide under realistic conditions. The role of humic substances. Water Rest, 19: 1229-1236,

Lay, J.P., W. Schauerte, W. Klein, and F. Korte. 1984. Influence of Tetrachloroethylene on the Biota of Aquatic Systems: Toxicity to Phyto- and Zooplankton Species in Compartments of a Natural Pond, Archives of Environmental Contamination & Toxicology, 13:135-142.

Lee, G.F. and R. Plumb. Literature Review on Research Study for the Development of Dredged Material Disposal Criteria, Contract report D-74-1. U.S. Army Engineer Waterways Expt. Sta., Vicksburg, MS, 1974.

Lee, G.F. and R.A. Jones. 1982. Discussion of: Dredged Material Evaluations: Correlation Between Chemical and Biological Evaluation Procedures, Journal of Water Pollution Control Federation, 54: 406-409.

Lee, H. 1992. Models, Muddles, and Mud: Predicting Bioacclumation of Sediments Associated Pollutants, *In:* 1229-1236. G.A. Burton (ed.) Sediment Toxicity Assessment, CRC-Lewis Publ., Boca Raton, FL. pp. 267-294.

Leonard, E.N., V.R. Mattson, D. Benoit, R. Hoke, and G. Ankley. 1993. Seasonal vartiation of acid volatile sulfide concentrations in sediment cores in Northeastern Minnesota. Hydrobiologia, 271: 87-95.

Leonard, E.N., A.M. Coter, and G.T. Ankley. 1995. Modified diffusion method for analysis of acid volatile sulfides and simultaneously extracted metals in freshwater sediments. Environ. Toxicol. Chem., 15: 1479-1481.

Lerman, A. and G. Brunskill. 1971. Migration of Major Constitints in Lake Sediments into Water and its Bearing on Lake Composition. Limnol. Oceanogr., 16: 886-887.

Liber, K., D.J. Call, T.P. Markee, K.L. Schmude, M.D. Balcer, F.W. Whiteman, and G.T. Ankley. 1996. Effects of Acid-Volatile Sulfide on Zinc Bioavailability and Toxicity to Benthic Macroinvertebrates: A Spiked-Sediment Field Experiment. Environmental Toxicology and Chemistry, 15: 2113 - 2125.

Lindstrom, R.M. and J.R. Moody. 1977. Selection and Cleaning of Plastic Containers for Storage for Trace Element Samples. Analytical Chemistry, 49: 2264-2267.

Long, E.R., M.F. Buchman, S.M. Bay, R.J. Breteler, R.S. Carr, P.M. Chapman, J.E. Hose, A.L. Lissner, J. Scott, and D.A. Wolfe. 1990. Comparative evaluation of five toxicity tests with sediments from San Francisco Bay and Tomales Bay, California. Environ. Toxicol. Chem., 9: 1193-1214.

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Management, 19: 81-97.

Long, E.R., L.J. Field, and D.A. MacDonald. 1998a. Predicting Toxicity in Marine Sedimants with Numerical Sediment Quality Guidelines. Environ. Toxicol. Chem., 17: 714-727.

Long, E.R., D.A. MacDonald, J.C. Cubbage, and C.G. Ingersoll. 1998b. Predicting the Toxicity of Sediment-Associated Trace Metals with Simultaneously Extracted Trace Metal: Acid-Volatile Sulfide Concentrations and Dry Weight-Normalized Concentrations: A Critical Comparison. Environ. Toxicol. Chem., 17: 972-974.

Loring, D.H. and R.T. Rantala. 1992. Manual for the Gechemical Analysis of Marine Sediments and Suspended Particulate Matter. Earth Sci. Rev., 32: 235-283.

Luoma, S.N. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci. Tot. Environ., 28: 1.

Luoma, S.N. 1989. Can We Determine The Biological Availability of Sediment-Bound Trace Elements? Hydrobiologia, 176/177: 379-396.

Luoma, S.N. and G.W. Bryan. 1982. A Statistical Study of Environmental Factors Controlling Concentrations of Heavy Meatals in the Burrowing Bivalve *Scrobicularia plana* and the Polychaete *Nereis diversicolor*. Estuarine, Coastal and Shelf Science, 15: 95-108.

Luoma, S.N. and G.W. Bryan 1978. Factors Controlling The Availability Of Sediment-bound Lead To The Estuarine Bivalve *Scrobicularia Plana*. Journal of the Marine Biological Assoc., 58: 793-802

Luoma, S.N. and J.A. Davis. 1983. Requirements For Modeling Trace Metal Partitioning In Oxidized Estuarine Sediments. Marine Chemistry, 12: 159-181.

Luoma, S.N. and E.A. Jenne. 1977. The availability of sediment-bound cobalt, silver, and zinc o a deposit feeding clam. *In*: Biological implications of metals in the Environment. R.E. Wilding and H. Drucker (eds.), Technical Information Center, Energy Research and Development Admin., Washington, D.C., pp. 213-220.

Luther, G.W. III, T.G. Ferdelman, J.E. Kostka, E.J. Tsamakis and T.M. Church. 1991. Temporal and Spatial Variability of Reduced Sulfur Species (FeS_2, $S_2O_3^{2-}$) and Porewater Parameters in Salt Marsh Sediments. Biogeochemistry, 14: 57-88.

Lyons, W.B., J. Gaudette, and G. Smith. 1979. Pore Water Sampling in Anoxic Carbonate Sediments: Oxidation Artifacts. Nature, 277: 48-49.

MacCrehan, W. and D. Shea. 1995. Temporal Relationship of Thiols to Inorganic Sulfur Compounds in Anoxic Chesapeake Bay. Sediment Porewater, *In*: M.D. Vairavamurty and

M.A.A. Schoohen eds. Geochemical Transformations of Sedimantary Sulfur. pp. 294-310. ACS Symposium Series 612, Washington DC.

MacRae, R.K. 1994. The Copper Binding Affinity of Rainbow Trout (*Oncorhynchus mykiss*) and Brook Trout (*Salvelihus fontinalis*) Gills. MS Thesis. U. Wyoming.

Maher, W.A. 1984. Evaluation of a Sequential Extraction Scheme to Study Associations of Trace Elements in Estuarine and Oceanic Sediments. Bull. Environ. Contam. Toxicol., 32: 339.

Mahoney, J.D., D. DiToro, A. Gonzalez, M. Curto, M. Dilg, L. DeRoss, and L. Sparrow. Partitioning of metals to sediment. Environ. Toxicol. Chem., 15: 2187-2197.

Malueg, K.W., G.S. Schuytema, J.H. Gakstatter, and D.F. Krawczyk. 1983. Effect of *Hexagenia* on *Daphnia* Response in Sediment Toxicity Tests. Environ. Toxicol. Chem., 2: 73-82.

Malueg, K.W., G.S. Schuytema, J.H. Gakstatter, and D.F. Krawczyk. 1984a. Toxicity of sediments from three metal contaminated areas. Environ. Toxicol. Chem., 3: 279-291.

Malueg, K.W., G.S. Schuytema, D.F. Krawczyk, and J.H. Gakstatter. 1984b. Laboratory sediment toxicity tests, sediment chemistry and distribution of benthic macroinvertebrates in sediments from the Keweenaw Waterway, Michigan, Environ. Toxicol. Chem., 3: 233-242.

Malueg, K.W., G.S. Schuytema, and D.F. Krawczyk. 1986. Effects of sample storage on a copper-spiked freshwater sediment. Environ. Toxicol. Chem., 5: 245-253.

McDonald, D.D. 1993. Development of an Approach to the Assessment of Sediments Quality in Florida Coastal Waters. MacDonald Environmental Sciences Ltd., VOR 2EO. Tallahassee, FL.

McDonald, D.D., E. Long, J. Field, C. Ingersoll, S. Carr, P. Haverland, T. Canfield, J. Dwyer, N. Kemble, F. Calder, G. Sloane, T. Seal, S. Smith, K. Keenleyside, C. Gaudet, M. Wong, and R. Fox. 1996. Application of ERLs and ERMs for Assessing Contaminated Sediments: Response to Sampson, Pastorok, and Ginn, SETAC News, September, pp. 31-34

Mahony, J.D., D.D. Toro, A. Gonzalez, M. Curto, M. Dilg, L. DeRoss, and L. Sparrow. 1996. Partitioning of metals to sediment organic carbon. Environ. Toxicol. Chem., 15: 2187-2197.

Manning, B.A. and S. Goldberg. 1997. Absorption Stability of As (III) at the Clay Mineral-Water Interface. Environ. Sci. Technol., 31: 2005-2011.

Marinsky, J.A. and J.H. Ephraim. 1986. A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids) 1. Analysis of the influence of polyelectrlyte properties on protonation equilibra in ionic media: Fundamental concepts. Environ. Sci. Technol., 20: 349-354.

Martin, W.R. and B.C. McCorkle. 1993. Dissolved organic carbon concentrations in marine pore waters determined by high temperature oxidation. Limnol. Oceanogr., 38: 1464-1479.

Martin, J.M. and M. Whitfield. 1981. The significance of the river input of chemical elements to the ocean, *In:* Trace Metals in Seawater, Proc. NATA Adv. Res. Inst. On Trace Metals in Seawater, ed. C.S. Wong. Plenium Press. New York.

Matisoff, G., O.P. Bricker, G.R. Holdren, and P. Kaerk. 1995. Spatial and Temporal Variations in the Interstitial Water Chemistry of Chesapeake Bay Sediments. *In*: Marine Chemistry in the Coastal Environment. pp. 343-363.

Matisoff, G., J.B. Fisher, and S. Matis. 1985. Effects of Benthic Macroinvertebrates on the Exchange of Solutes between Sediments and Freshwater. Hydrobiologia, 122: 19-33.

Matisoff, G. and J. Robbins. 1987. A Model for Biological Mixing of Sediments. J. Geological Education, 35: 144-149.

Mayer, L.M. 1976. Chemical water sampling in lakes and sediments with dialysis bags. Limnology & Oceanography, 29: 617-673.

MDA Environmental Ltd. 1997 draft. Technical Evaluation of Pore Water, Sediment Digestion of Metals, Background Concentration of Metals and Sediment, and Sample Handling. Hamilton Ontario.

Meinelt, T, R. Krueger, M. Pietruck, R. Osten, and C. Steinberg. 1997. Mercury Pollution and Macrophage Centers in Pike (*Esox lucius*) Tissues. Environ. Sci. Pollut. Res., 4: 32-36.

Miller, M.P and A.C. Hendricks. 1996. Zinc Resistance in *Chironomus riparius* for Physiological and Genetic Components, J. N. Am. Benthol. Soc., 15: 106-116.

Millero, F.J., S. Hubinger, M. Fernandez, and S. Garrett. 1987. Oxidation of H_2S in Seawater as a Function of Temperature, pH, and Ionic Strength. Environ. Sci. Technol., 21: 439-443.

Mills, A.L. and R.N. Cowell. 1977. Microbiological Effects of Metal Ions in Chesapeake Bay Water and Sediments. Bull. Environ. Contam. Toxicol., 18: 99-103.

Morrisey, D. J., A.J. Underwood, and L. Howitt. 1996. Effects of Cu on the Faunas of Marine Soft-Sediments: An Experimental Field Study, Marine Biology, 125: 199-213.

Morse, J.W., F.J. Millero, J.C. Cornwell, and D. Rickard. 1987. The Chemistry of the Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters. Earth Science Rev., 24: 1-42.

Mudroch, A. and S.D. MacKnight. 1991. Handbook of Techniques for Aquatic Sediment Sampling. CRC Press, Boca Raton, FL, 210 pp.

Muir, D.C.G., N.D. Griff, B.E. Townsend, D.A. Matner, and W.L. Lockhart. 1982. Comparison of the Uptake and Bioconcentration of Fluridone and Terbutryn by Rainbow Trout and *Chironomus tentans* in Sediment and Water Systems. Archiv. Environ. Contam. Toxicol.,11: 595-602.

Muir, D.C.G., B.E. Townsend, and W.L. Lockhart. 1983. Bioavailability of Six Organic Chemicals to *Chironomus tentans* Larvae in Sediment and Water. Environ. Toxicol. Chem., 2: 269-281.

Muir, D.C.G., G.P. Rawn, B.E. Townsend, W.L. Lockhart, and R. Greenhalgh. 1985. Bioconcentration of Cypermethrin, Deltamethrin, Fenvalerate and Permethrin by *Chironomus tentans* Larvae in Sediment and Water. Environ. Toxicol. Chem., 4: 51-61.

Munger, C. and L. Hare. 1997. Relative importance of water in food as cadmium sources to an aquatic insect (*Charoborus punctipennis*): Implications for predicting cadmium bioacclumation in nature. Environ. Sci. Technol., 31: 891-895.

Murray, J.W. and L.U. Grundmanis. 1980. Hydrogen Consumption in Pelagic Marine Sediments. Sci. 209: 1527-1530.

Murray, W.G. and J. Murray. 1987. A device for obtaining representative samples from the sediment-water interface. Marine Geology, 76: 313-317.

Nebeker, A.V., S.T. Onjukka, M.A. Cairns, and D.F. Krawczyk. 1986. Survival of *Daphnia magna* and *Hyalella azteca* in cadmium spiked water. Environ. Toxicol. Chem., 5: 933-938.

Nelson, M.K., P.F. Landrum, G.A. Burton, S.J. Klaine, E.A. Crecelius, T.D. Byl, D.C. Gossiaux, V.N. Tysmbal, L. Cleveland, C.G. Ingersoll and G. Sasson-Brickson. 1993. Toxicity of contaminated sediments in dilution series with control sediments. Chemosphere, 27: 1789-1812.

Newman, M.C. and C.H. Jagoe. 1994. Ligands and the bioavalibility of metals in aquatic Environments. *In*: J.L. Hamelik, P.I. Lardin, H.L. Bergemann, and W.H. Benson (eds.). Bioaval., Physical, Chemical, and Biological Interactions. 17: 39-61. Lewis Publ., Boca Raton, FL.

Nirel, P.M.V. and F.M.M. Morel. 1990. Pitfalls of sequential extractions. Water Res., 24: 1055-1056.

NOAA, 1987. Collection of Bivalve Molluscs and Surficial Sediments, and Performance of Analysis for Organic Chemicals and Toxic Trace Elements, Phase I Final Report, National Statistics and Trends Mussel Watch Program, Prepared by Battelle Ocean Sciences for the National Oceanic and Atmospheric Administration, Rockville, MD, 1987.

Nyffeler, U.P., Y. Li, and P. Santgchi. 1984. A Kinetic Approach to Describe Trace Element Distribution Between Particles and Solution in Natural Aquatic Systems. Geochemical et Cosmochmica Acta, 48: 1513-1522.

Oakley, S.M., P.O. Nelson, and K.J. Williamson. 1981. Model of trace-mutual partitioning in marine sediments. Environ. Sci. Technol., 15: 474-480.

O'Donnel, J.R., B.M. Kaplan, and H.E. Allen. 1985. Bioavailability of trace metals in natural waters. Aquatic Toxicol. and Hazard Assessment: Seventh Symposium. ASTM STP 854, ASTM, Philadelphia, PA, pp. 485-501.

O'Neill, E.J., C.A. Monti, P.H. Prichard, A.W. Bourquin, and D.G. Ahearn. 1985. Effects of Lugworms and Seagrass on Kepone (Chlordecone) Distribution in Sediment-Water Laboratory Systems. Environ. Toxicol. Chem., 4: 453-458.

Oscaron, D.W., P.M. Huang, C. Defosse, and A. Herbillon. 1981. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. Nature, 291: 50-51.

Papelis, G., K.I. Hayes, and J.O. Leckie. 1988. HYDRAQL: A Program for the Computation of Chemical Equilibrium Composition of Aqueous Batch Systems Including Surface –

Complexation Modeling in Iron Adsorption at the Oxide/Solution Interface. Dept. Civil Eng. Standford U. Standford, CA.

Pascoe, G.A. and J.A. DalSoglio. 1994. Planning and Implementation of a Comprehensive Ecological Risk Assessment at the Milltown Reservoir – Clark Fork River Superfund Site, Montana. Environ. Toxicol. Chem., 13: 1943-1956.

Pascoe, G.A., R.J. Blanchet, G. Linder, D. Palawski, W.G. Brumbaugh, T. L. Canfield, N.E. Kemble, C.G. Ingersoll, A. Farag, and J.A. DalSoglio. 1994. Characterization of Ecological Risks at the Milltown Reservoir – Clark Fork River Sediments Superfund Site, Montana. Environ. Toxicol. Chem., 13: 2043-2058.

Pastorok, R.A. and D.S. Becker. 1990. Comparative sensitivity of sediment toxicity bioassays at three superfund sites in Puget Sound, pp. 123-139. W.G. Landis and W.H. van der Schalie (eds.). Aquatic Toxicology and Risk Assessment: 13th Vol., ASTM STP 1096, American Soc. Testing and Materials, Philadelphia, PA.

Patrick, W.H., Jr. 1964. Extractable Iron and Phosphorus in Submersed Soil at Controlled Redox Potential. Trans. 8th Intern Congress on Soil Science, 4: 605-609.

Pedersen, S.N., P.K. Lundebye, and M.H. Depledge. 1997. Field Application of Metallothionein and Stress Protein Biomarkers in the Shore Crab (*Carcinus maenas*) Exposed to Trace Metals. Aquatic Toxicology, 37: 183-200.

Perin, G., R. Fabris, S. Manente, A.R. Wagner, C. Hammacher, and S. Scotto. 1997. A Five-Year Study on the Heavy-Metal Pollution of Guanabara Bay Sediments (Rio de Janeiro, Brazil) and Evaluation of the Metal Bioavailability By Mean of Geochemical. Water Research, 31: 3017-3028

Pesch, C.E., D.J. Hansen, W.S. Boothman, W.J. Berry, and J.D. Mahony. 1995. The Role of Acid-Volatile Sulfide and Interstitial Water Metal Concentrations in Determining Bioavailability of Cadmium and Nickel From Contaminated Sediments to the Marine Polychaete *Neathes arenaceodentata*. Environmental Toxicology and Chemistry, 14: 129-141.

Peterson, G.S., G.T. Ankley, and E.N. Leonard. 1996. Effect of Biotrubation on Metal-Sulfide Oxidation in Surficial Freshwater Sediments. Envionmental Toxicology and Chemistry, 15: 2147-2155.

Pittinger, C.A., V.C. Hand, J.A. Masters, and L.F. Davidson. 1988. Interstitial Water Sampling in Ecotoxicological Testing: Partitioning of a Cationic Surfactant, Toxicology and Hazard Assessment, 10: 138-148.

Plumb, R.H., Jr., 1980. Sampling, Preservation, and Analysis of Sediment Samples: State-of-the-Art Limitations, Proceedings Fifth United States-Japan Experts Meeting on Management of Bottom Sediments Containing Toxic Substances, New Orleans, LA (1979), U.S. EPA/60019-80-044, pp. 259-272.

Plumb, R.H., Jr. 1981. Procedures for handling and chemical analyses of sediment and water samples. Technical Report U.S. EPA/CE-81-1. U.S. Army Corps of Engineers, Vicksburg, MS.

Pritchard, P.H., C.A. Monti, E.J. O'Neill, J.P. Connolly, and D.G. Ahearn. 1986. Movement of Kepone (Chlordecone) Across an Undisturbed Sediment-Water Interface in Laboratory Systems, Environmental Toxicology & Chemistry, 5: 647-657.

Rapin, F., A. Tessier, P.G.C. Campbell, and R. Carigen. 1986. Environ. Sci. Technol., 20: 836-840.

Reeburgh, W.S. 1967. An Improved Interstitial Water Sampler, Limnology & Oceanography, 12: 163-165.

Reichert, W.L., B. Le Eberhart, and U. Varanasi. 1985. Exposure of Two Species of Deposit-Feeding Amphipods to Sediment-Associated [3H]benzoapyrene: Uptake, Metabolism and Covalent Binding to Tissue Macromolecules, Aquatic Toxicology, 6: 45-56.

Revsbech, N.P., B.B. Jorgensen, T.H. Blackburn, and Y. Cohen. 1983. Microelectrode Studies of the Photosynthesis, oxygen, H_2S and pH Properties of a Microbial Matter. Limnol. Oceanogr., 28: 1062-1074.

Rochon, R. and M. Chevalier. 1987. Sediment Sampling and Preservation Methods for Dredging Projects. Conservation and Protection-Environment Canada, Quebec Region.

Rosenfeld, J.K. 1979. Ammonia absorption in nearshore anoxic sediments. Limnol. Oceanogr., 24: 356-364.

Ross, P.E. and M.S. Henebry. 1989. Use of four microbial tests to assess the ecotoxicological hazard of contaminated sediments. Tox. Assess., 4: 1-21.

Rubinstein, N.I., E. Lores, and N.R. Gregory. 1983. Accumulation of PCBS, Mercury and Cd by *Nereis virens, Mercenaria mercenaria* and *Palaemonetes pugio* from Contaminated Harbor Sediments. Aquatic Toxicology, 3: 249-260.

Rutledge, P.A. and J. Fleeger. 1988. Laboratory studies on core sampling with application to subtidal meiobenthos collection. Limnology and Oceanography, 33: 274-280.

Saager, P.M., J-P Sweerts, and H.J. Ellermeijer. 1990. A simple pore-water sampler for coarse, sandy sediments of low porosity. Limnol. Oceanogr., 35: 747-751.

Salomons, W. 1985. Sediments and water quality. Sci. Technol. Lett., 6: 315-326.

Salomons, W. and U. Förstner. Trace Metal Analysis on Polluted Sediment. II. Evaluation of Environmental Impact, Environmental Technology Letters, 1: 506-517.

Santschi, P.H., V.P. Nyffeler, P. O'Hara, M. Buchholtz, and W.S. Broecker. 1984. Radiotracer uptake on the seafloor: Results from the MANOP chamber deployments in the eastern Pacific. Deep-Sea Res., 31: 451-468.

Sarda, N. and G.N. Burton, Jr. 1995. Ammonia variation in sediments: spatial, temporal and method-related effects. Environ. Toxicol. Chem., 14: 1499-1506.

Sander, G., J. Hamilton-Tayor, and K.C. Jones. 1996. PCB and PAH dynamics in a small rural lake. Environ. Sci. Technol., 30: 2958-2966.

Sasson-Brickson, G. and G.A. Burton Jr. 1991. *In Situ* and Laboratory Toxicity Testing With *Ceriodaphnia dubia*. Environ. Toxicol. Chem., 10: 201-207.

Sayles, F.L., T.R.S. Wilson, D.N. Hume, and P.C. Mangelsdorf Jr. 1973. In situ sampler for marine sedimentary pore waters: Evidence for potassium depletion and calcium enrichment. Science, 180: 154-156

Schecher, W.D. and W. McAvoy. 1994. MINEQL and, Users Manual. Environmental Resource Software. Hallowell, ME.

Schindler, P.W. 1975. Removal of trace metals from the oceans: a zero order model. Thalassia Jogos Pavica, 11: 101-111.

Schindler, P.W. 1981. Surface Complexns of Oxide-Water interfaces, In Absorption of Inorganics at Solid-Liquid Interfaces. Ed. By M.A. Anderson and A.J. Rubin. Ann Arbor Sci. Publisher. Ann Arbor, MI. pp. 1-49.

Schubauer-Berigan, M.K. and G.T. Ankley. 1991. The contribution of ammonia, metals and nonpolar organic compounds to the toxicity of sediment pore water from an Illinois River tributary. Environ. Toxicol. Chem., 10: 925-939.

Schults, D.W., S.P. Ferraro, L.M. Smith, F.A. Roberts, and C.K. Poindexter. 1992. A Comparison Of Methods For Collecting Interstitial Water For Trace Organic Compounds And Metals Analyses. Water Res., 26: 989-995.

Schuytema, G.S., P.O. Nelson, K.W. Malueg, A.V. Nebeker, D.F. Krawczyk, A.K. Ratcliff, and J.H. Gakstatter. 1984. Toxicity of Cd in Water and Sediment Slurries *to Daphnia magna*. Environmental Toxicology & Chemistry, 3: 293-308.

Sherman, L.A., L.A. Baker, E.P. Weir, and P.L. Brezonik. 1994. Sediment Pore Water Dynamics of Little Rock Lake, Wisc.: Geochemical Processes and Seasonal and Spatial Variability. Limnol. Oceanogr., 39: 1155-1171.

Sibley, P.K., G.T. Ankley, A.M. Cotter, and E.N. Leonard. 1996. Predicting Chronic Toxicity of Sediments Spiked With Zinc: An Evaluation of the Acid-Volatile Sulfide Model Using A Life-Cycle Test With the Midge *Chironomus tentans*. Environ. Toxicol. Chem., 15: 2102-2112.

Silver, M. L. 1972. Handling and Storage of Chemically and Biologically Active Ocean Sediments, MTS J., 6 :32-36.

Simon, N.S., M.M. Kennedy, and C.S. Massoni. 1985. Evaluation and Use of a Diffusion Controlled Sampler for Determining Chemical and Dissolved Oxygen Gradients at the Sediment-Water Interface. H ydrobiologia, 126:135-141.

Simpson, S.L., S.C. Apte, and G.E. Batley. 1998. Effect of Short-Term Resuspension Events on Trace Metal Speciation in Polluted Anoxic Sediments, Environmental Science & Technology, 32: 620-625.

Singh, S.K., Narwal, and V. Subramanian. 1984. Hydrous Fe and Mn Oxides – Scavengers of Heavy Metals in the Aquatic Environment. Crit. Rev. Env. Publ., 14: 33-90.

Skalski, C. 1991. Laboratory and In Situ Sediment Toxicity Evaluations Using Early Life Stages of *Pimephales promelas*. M.S. thesis. Wright State University, Dayton, OH.

Sly, P.G. 1969. Bottom Sediment Sampling, Proceedings of 12th Conference Great Lakes Research, pp. 883-898.

Smith, R.W. and E.A. Jenne. 1991. Recalculation, Evaluation, and Prediction of Surface Complexats Constants for Metal Absorption on Iron and Manganese Oxides. Environ. Sci. Technol., 25: 525-531.

Stemmer, B.L., G.A. Burton, Jr., and S. Leibfritz-Frederick. 1988. Effect of Sediment Test Variables on Se Toxicity to *Daphnia magna*, Environ. Toxicol. Chem., 9: 1035-1044.

Stemmer, B.L. , G. Sasson Brickson, and G. A. Burton. 1990. Effect of Sediment Spatial Variance and Collection Method on Cladoceran and Microbial Activity Determinantions. Environ. Toxicol. Chem., 9: 1035-1044.

Stephenson, R.R. and D.F. Kane. 1984. Persistence and Effects of Chemicals in Small Enclosures in Ponds. Archives of Environmental Contamination & Toxicology, 13: 313-326.

Stephenson, R.R. and M.A. Turner. 1993. A Field Study of Ecological Dynamics in Perphyton and in *Hyalella azteca.* Water, Air, Soil Pollut., 68: 341-361.

Suedel, B.C., J.H. Rodgers,Jr. and P.A. Clifford.1993. Bioavailability of fluoranthene in freshwater sediment toxicity tests. Environ. Toxicol. Chem., 12: 155-165.

Sundby, B. and N. Silverberg. 1985. Manganese Fluxes in the Benthic Boundary Layer, Limnol. Oceanogr., 30: 372-381.

Swartz, R.C., W.A. DeBen, J.K. Jones, J.O. Lamberson, and F.A. Cole. 1985a. Phoxocephalid amphipod bioassay for marine sediment toxicity. Aquatic Toxicol. and Hazard Assessment, Seventh Symposium, ASTM STP 854, Philadelphia, PA. pp. 284-307.

Swartz, R.C., G.R. Ditsworth, D.W. Schults, and J.O. Lamberson. 1985b. Sediment Toxicity to a Marine Infaunal Amphipod: Cd and Its Interaction with Sewage Sludge. Marine & Environ. Res., 18: 133-153.

Swartz, R.C. 1987. Toxicological Methods for Determining the Effects of Contaminated Sediment on Marine Organisms, Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems, Pergamon Press, New York, pp. 183-198.

Swartz, R.C., P.F. Kemp, D.W. Schults, G.R. Ditsworth, and R.J. Ozretich. 1989. Acute toxicity of sediments from Eagle Harbor, Washington, to the infaunal amphipod, *Rhepoxynius abronius*. Environ. Toxicol. Chem., 8: 215-222.

Swartz, R.C., D.W. Schults, T.H. DeWitt, G.R. Ditsworth and J.0. Lambertson. 1990. Toxicity of fluoranthene in sediment to marine amphipods: a test of the equilibrium partitioning approach to sediment quality criteria. Environ. Tox. Chem., 9: 1071-1080.

Tatem, H.E. 1988. Use of *Daphnia magna* and *Mysidopsis almyra* to Assess Sediment Toxicity," Water Quality '88, Seminar Proceedings, Charleston, S.C., U.S. Army Corps of Engineers Committee on Water Quality, Washington, DC.

Tay, K.L., K.G. Doe, S.J. Wade, D.A. Vaughan, R.E. Berrigan, and M.J. Moore. 1992. Sediment bioassessment in Halifax Harbor. Environ. Toxicol. Chem., 11: 1567-1581.

Teasdale, P., S. Apte, G. Batley, and P. Ford. 1996. Mount Lyell Remediation; The behaviour of copper in sediments and waters of Macqaire Harbour, Western Tasmaina, Supervising Scientist Report. pp. 1-118

Teasdale, P.R., G.E. Bately, S.C. Apte, and I.T. Webster. 1995. Pore Water Sampling With Sediment Peepers, Trends in Analytical Chemistry, 14: 250-256.

Tessier, A., Y. Couillard, P.G.C. Campbell, and J.C. Auclair. 1993. Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve *Anodonta grandis* Limnol. Oceanogr., 38: 1-17

Tessier, A., R. Carignan, N. Belzile, D. Fortin, R.R. DeVitre, and G.G. Leppard. 1996. Metal Sorption to Diagenetic Iron and Mn Oxyhydoxides and Associated Organic Matter: Narrowing the Gap Between Field and Lab Measurements. Geochem. Cosmochim et Acta, 60: 387-404.

Tessier, A., R. Carignan, B. Dubreuil, and F. Rapin. 1989. Partitioning of zinc between the water column and the oxic sediments in lakes. Geochem. Cosmochem. Acta, 53: 1511-1522.

Tessier, A., P.G.C. Campbell, J.C. Auclair., and M. Bisson. 1984. Relationships Between the Partitioning of Trace Metals in Sediments and Their Accumulation in the Tissoes of the Freshwater Mollusc *Elliptio complanata* in a Mining Area, Canadian Journal of Fish and Aquatic Science, 41: 1463-1472.

Tessier, A., D. Cambell, and M. Bisson. 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Analytical Chemistry, 51: 844-851.

Tessier, A. and P.G.C. Campbell. 1987. Partitioning of trace metals in sediments: relationships with bioavailability. Hydrobiologia, 149: 43-52

Tessier, A. and P.G.C. Campbell. 1988. Comments on the testing of the accuracy of an extraction procedure for the partitioning of trace metals in sediments. Analytical Chem., 60: 1475-1476.

Tessier, A. and P.G.C. Campbell. 1991. Comments on "Pitfalls of Sequential Extentions," by PMV Nivel and FMM Morell. Water Res., 25: 115-117.

Tessier, A. and D.R. Turner. (eds.) 1995. Metal Speciation and Bioavailability in Aquatic Systems. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. John Wiley and Sons, New York.

Thomson, E.A. *et al.* 1980. The Effect of Sample Storage on the Extraction of Cu, Zn, Fe, Mn and Organic Material form Oxidized Estuarine Sediments. Water, Air, and Soil Pollution, 4: 51-61.

Tipping, E. 1994. WHAM. A Chemical Equilibrium Model and Computer Code for Waters, Sediments, and Soils Incorporating a Discrete Site/Electrostatic Model of Ion-Binding by Humic Substances. Comp. Geo. Sci., 20: 973-1023.

Tipping, E. and M.A. Hurley. 1992. A Unifying Model of Cation Binding by Humic Substances. Geochem. Cosmochem. Acta, 56: 3627-3641.

Troup, B.N., O.P. Bricker, and J.T. Bray. 1974. Oxidation effect on the analysis of iron in the interstitial water of recent anoxic sediments. Nature, 249: 237-239.

Tsushimoto, G., F. Matsumura, and R. Sago. 1982. Fate of 2, 3, 7, 8-tetrachlorodebenzo-p-dioxin (TCDD) in an Outdoor Pond and in Model Aquatic Ecosystems. Environ. Toxicol. Chem., 1: 61-68.

Ulman, W.J. and R.C. Aller. 1982. Diffusion Coefficent in Nearshore Marine Sediments. Limnol. Oceanogr., 27: 352-359.

U.S. Army Corps of Engineers 1976. Ecological Evaluation of Proposed Dredged or Fill Material into Navigable Water. Misc. Paper. D-76-17.

U.S. Environmental Protection Agency. 1982a. Sampling Protocols for Collecting Surface Water, Bed Sediment, Bivalves, and Fish for Priority Pollutant Analysis, Final Draft Report, Office of Water Regulations and Standards Monitoring and Data Support Division, Washington, D.C.

U.S. Environmental Protection Agency. 1982b. Handbook for Sampling and Sample Preservation of Water and Wastewater, Environment Monitoring and Support Lab, Cincinnati, EDA-600/4-82-029.

U.S. Environmental Protection Agency, Region 10. 1986. Recommended Protocols for Conducting Laboratory Bioassays on Puget Sound Sediments, Puget Sound Estuary Program, Prepared by TetraTech, Inc. and E.V.S. Consultants, Inc., Final Report TC-3991-04, U.S. EPA, Seattle, Washington.

U.S. Environmental Protection Agency. 1987. A Compendium of Superfund Field Operation Methods, Office of Emergency and Remedial Response, Washington, D.C., U.S. EPA/540-P-87/001.

U.S. Environmental Protection Agency. 1991a. Methods for aquatic toxicity identification evaluations: Phase I toxicity characterization procedures. 2nd ed. U.S. EPA/600/6-91-003. Environmental Research Laboratory, Duluth, MN.

U.S. Environmental Protection Agency. 1991b. Methods for aquatic toxicity identification evaluations: Phase II toxicity characterization procedures. 2nd ed. U.S. EPA/600/6-91-004. Environmental Research Laboratory, Duluth, MN.

U.S. Environmental Protection Agency. 1991c. Methods for aquatic toxicity identification evaluations: Phase III toxicity characterization procedures. 2nd ed. U.S. EPA/600/6-91-005. Environmental Research Laboratory, Duluth, MN.

U.S. Enviromnental Protection Agency/U.S. Army Corps of Engineers. 1991d. Evaluation of dredged material proposed for ocean disposal (Testing Manual). U.S. EPA 503/8-91-001. Washington, DC.

Van Rees, K.C.J., E.A. Sudlicky, P. Suresh, C. Rao, and K. Ramesh Reddy. 1991. Environmental Science and Technology, 25: 1605-1611.

Visscher, P.T., J. Beukema, and H. van Gemerden. 1991. *In situ* characterization of sediments: measurements of oxygen and sulfide profiles with a novel combined needle electode. Limnol. Oceanogr., 36: 1476-1480

Wall, S.B., J. J. Isley, and T.W. La Point. 1996. Fish Bioturbation of Cd-Contaminated Sediments: Factors Affecting Cd Availability to *Daphnia magna*. Environ. Toxicol. Chem., 15: 294-298.

Wang, F., J. Clen, and W. Forsling. 1997. Modeling Sorption of Trace Metals on Natural Sediments by Surface Complexation Model. Environ. Sci. Technol., 31: 448-453.

Wang, Xiaosong and G. Matisoff 1997. Solute Transport in Sediments by a Large Freshwater Oligochaete, *Branchiura sowerbyi*", Environmental Science & Technology, 31: 1926-1933.

Watson, P.G., P. Frickers, and C. Goodchild. 1985. Spatial and Seasonal Variations in the Chemistry of Sediment Interstitial Waters in the Tamar Estuary. Estuaries & Coastal Shelf Science, 21: 105-119.

Watson, P.G., and T.E. Frickers. 1990. A multilevel, *in situ* pore -water sampler for use in intertidal sediments and laboratory microcosms. Limnol. Oceanogr., 35: 1381-1389.

Webster, I.T., P.R. Teasdale and N.J. Grigg. 1998. Theoretical and Experimental Analysis of Peeper Equilibration Dynamics, Environmental Science & Technology, 32: 1727-1733.

Wenholz, M. and R. Crunkilton. 1995. Use of toxicity identification evaluation procedures in the assessment of sediment pore water toxicity from an urban stormwater retention pond in Madison, Wisconsin. Bull. Environ. Contam. Toxicol., 54: 676-682.

Whiteman, F., G. Ankley, M. Kahl, D. Rau, and M.Balcer. 1996. Evaluation of Interstitial Water as a Route of Exposure for Ammonia in Sediment Tests with Benthic Macroinvertebrates. Environmental Toxicology and Chemistry, 15: 794-801.

Whitman, R.L. 1989. A new sampler for collection of interstitial water from sandy sediments. Hydrobiologia 176/177: 531-533.

Wilkness, P.E. and R.A. Carr. 1973. Mercury: A Short-Term Storage of Natural Waters. Environmental Science and Technology, 7: 62-63.

Winger, P.V. and P.J. Lassier. 1991. A vacuum-operated pore-water extractor for estuarine and freshwater sediments. Arch. Environ. Contam. Toxicol., 21: 321-324.

Wolfe, N.L., B.E. Kitchen, D.L. Maclady, and T.J. Grundl. 1986. Physical and Chemical Factors that Influence the Anaerobic Degradation of Methylparathion in Sediment Systems. Environmental Toxicology and Chemistry, 5: 1019-1026.

Wood, L. W., C.Y. Rhee, B. Bush, and E. Barnard. 1987. Sediment Desorption of PCB Congeners and Their Bio-Uptake by Dipteran Larvae. Water Research, 21: 873-884.

Woodward, D.F., W.G. Brumbaugh, A.J. DeLonay, E.E. Little, and C.E. Smith. 1993. Effects on Rainbow Trout of a Metal Contaminated Diet of Benthic Invertebrates from the Clark Fork River, Montana. Trans. Amer. Fish. Soc., 123: 51-62.

Word, J. Q., J.A. Ward, L.M. Franklin, V.I. Cullinan, and S.L. Kiesser. 1987. Evaluation of the Equilibrium Partitioning Theory for Estimating the Toxicity of the Nonpolar Organic Compound DDT to the Sediment Dwelling Amphipod *Rhepoxynius abronius.* Battelle/Marine Research Laboratory Report, Task 1, WA56, Sequim, Washington, 60 pp.

Zar, J.H. 1984. Biostatistical Analysis. 2nd Edition, Prentice-Hall, Inc., N.J. 718 pp.

Zhuang, Y., H.E. Allen, and G. Fu. 1994. Effect of aeration of sediment on cadmium binding. Environ. Toxicol. Chem., 13: 717-724.

Appendix

Additional Reference Materials

Abu-Saba, K.E. and A.R. Flegal. 1997. Temporally Variable Freshwater Sources of Dissolved Cr to the San Francisco Bay Estuary. Environmental Science and Technology, 31: 3455-3460.

Ahmann, D., L.R. Krumholz, H.F. Hemond, D.R. Lovley, and F.M.M. Morel. 1997. Microbial Mobilization of As from Sedimants of the Aberjona Watershed. Environmental Science and Technology, 31: 2923-293.

Alldredge, J.R. 1987. Environmental Monitoring and Assessment, 9: 143-154.

Allen, H.E. and C.P. Huang. 1996. Predicting soil - water partition coefficients for Cd. Environmental Science and Technology, 30: 3418-3422.

Andersen, F.0. and W. Helder. 1987. Comparison of Oxygen Microgradients, Oxygen Flux Rates and Electron Transport System Activity in Coastal Marine Sediments. Marine Ecology Progress Series, 37: 259-264.

Anderson, J., W. Birge, J. Gentile, J. Lake, J. Rodgers, Jr., and R. Swartz. 1987. Biological Effects, Bioaccumulation, and Ecotoxicology of Sediment-Associated Chemicals, Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems, Pergamon Press, New York, pp. 267-296.

Ankley, G.T., G.L. Phipps, E.N. Leonard, D.A. Benoit, and V.R. Mattson. 1991. Acid-Volatile Sulfide as a Factor Mediating Cadmium and Nickel Bioavailability in Contaminated Sediments. Environmental Toxicology and Chemistry, 10: 1299-1307.

Anonymous. 1992. The Impact of Transport and Storage Temperature on Sample Integrity. The Hazardous Waste Consultant . July/ Aug. pp. 1.3-1.5.

Apte, S.C. and G.E. Batley. 1995. Trace Metal Speciation of Labile Chemical Species in Natural Waters and Sediments: Non-Electrochemical Approaches. Metal Speciation and Bioavailability in Aquatic Systems. Ed. A. Tessier and D. R. Turner. John Wiley and Sones, Ltd. pp. 259-306.

Archer, D. and A. Devol. 1992. Benthic Oxygen Fluxes in the Washington Shelf and Slope: A Comparison of *in situ* Microelectrode and Chamber flux measurements. Limnology and Oceanography, 37: 614-629.

ASTM. 1995. D 3976-92 Standard practice for preparation of sediment samples for chemical analysis, pp. 163-165. *In*: ASTM Standards on Environmental Sampling, Philadelphia, PA.

Becker, D, Scott and T.C. Ginn. 1995. Effects of Storage Time on Toxicity of Sediments from Puget Sound, Washington. Environmental Toxicology and Chemistry, 14: 829-835.

Bennett, J.R. 1987. The Physics of Sediment Transport, Resuspension, and Deposition. Hydrobiologia, 149: 5-12.

Bennett, W.A., A. Sosa, and T.L. Beitinger. 1995. Oxygen Tolerance of Fathead Minnows Previously Exposed to Copper. Bulletin of Environ. Contam. Toxicol., 55: 517-524.

Benoit, D.A., G.L. Phipps, and G.T. Ankley. 1993. A Sediment Testing Intermittent Renewal System for the Automated Renewal of Overlying Water in Toxicity Tests with Contaminated. 27: 1403-1412.

Blomqvist, S. 1991. Quantitative Sampling of Soft-Bottom Sedimants: Problems and Solutions. Marine Ecology Progress Series. 72: 295-304.

Blomqvist, S. and B. Abrahamsson. 1987. A Device for Rapid Sectioning of Soft Bottom Sediment Cores. Schweizerische Zeitschrift fur Hydrologie, 49: 393-396.

Blomqvist, S. and K. Bostrom. 1987. Improved Sampling of Soft Bottom Sediments by Combined Box and Piston Coring. Sedimentology, 34: 715-719.

Bonzongo, J.-C. J., K.J. Heim, Y. Chen, W.B. Lyons, J.J. Warwick, G.C. Miller, and P.J. Lechiler. 1996. Mercury Pathways In The Carson River-Lathontan Reservoir System. Nevada, USA. Environmental Toxicology and Chemistry, 15: 677-683.

Brannon, J. and W. Patrick, Jr. 1987. Fixation, Transformation, and Mobilization of Arsenic in Sediments. Environ. Sci. Technol., 32: 450-459.

Breault, R.F., J.A. Colman, G.R. Aiken, and D. McKnight. 1996. Copper Speciation and Binding by Organic Matter in Copper-Contaminated Streamwater. Environmental Science and Technology, 30: 3477-3486.

Brumbaugh, W.G. and J.W. Arms. 1996. Quality Control Considerations for the Determination of Acid-Volatile Sulfide and Simultaneously Extracted Metals in Sediments. Environmental Science and Chemistry, 15: 282-285.

Burgess, M., B.A. Rogers, S.A. Rego, J.M. Corbin, and G.E. Morrison. 1994. Sand Spiked with Copper as a Reference Toxicant Material for Toxicity Testing: A Preliminary Evaluation. Archives of Environmental Contamination and Toxicology, 26: 163-168.

Busatti, B., A. Magagnoli, M. Mengoli, and S. Guerzoni. 1988. Environmental Technology Letters, 9: 375-378.

Carroll, S.A., P.A. O'Day, and M. Piechowski. 1998. Rock-Water Interactions Controllong Zinc, Cadmium, and Lead Concentrations in Surface Waters and Sediments, U.S. Tri-State Mining District 2. Geochemical Interpretation. Environmental Science and Technology, 32: 956-965.

Cain, D.J., S.N. Luoma, J.L. Carter, and S.V. Fend. 1992. Aquatic Insects as Bioindicators of Trace Element Contamination In Cobble-Bottom Rivers and Streams. Canadian Journal of Fish and Aquatic Science, 49: 2141-2154.

Campbell, P.G.C. and A. Tessier. 1996. Ecotoxicity of metals in the aquatic Environment: geochemical aspects. *In:* M.C. Neuman and C.H. Jagoe (eds.). Ecotoxicology: A Hierarchical Treatment. Lewis Publishers, Boca Raton, FL.

Chapman, P.M. 1987. Marine sediment toxicity tests. *In*: Symposium on Chemical and Biological Characterization of sludges, Sediments, Dredge Spoils and Drilling Muds. ASTM STP 976, American Society for Testing and Materials, Philadelphia, pp. 391-402.

Chapman, P.M., H.E. Allen, K. Godtfredsen, and M.N. Z'Graggen. 1996. Evaluation of Bioaccumulation Factors in Regulating Metals. Environ. Sci. Technol., 30: 448-452.

Chao, T.T. and L. Zhou. 1983. Extraction Techniques for Selective Dissolution of Amorphous Iron Oxides from Soils and Sediments. Soil Science Society of America Journal, 47: 225-232.

Chau, A.S.Y. and H.-B. Lee. 1980. Analytical Reference Materials. III. Preparation and Homogeneity Test of Large Quantities of Wet and Dry Sediment Reference Materials for Long Term Polychlorinated Biphenyl Quality Control Studies. Association of Official Analytical Chemists, Inc., 63: 947-651.

Clifford, H.F. and R.J. Casey. 1992. Differences Between Operators in Collecting Quantitative Samples of Stream Macroinvertebrates. Journal of Freshwater Ecology, 7.

Cowan, C.E., J.M. Zachara, and C.T. Resch. 1991. Cadmium Adsorption on Iron Oxides in the Presence of Alkaline-Earth Elements. Environ. Sci. Technol., 25: 437-446.

de Carvalho, Paulo Sergio Martins, Eliete Zanardi, S. Buratini, M.C. Lamparelli, and M.C. Martins. 1998. Oxidizing Effect on Metal Remobilization and *Daphnia similis* Toxicity from a Brazilian Reservoir Sediment Suspension. Elsevier Science Ltd., 32: 193-199.

Diamond, J.M., D.G. Mackler, W.J. Rasnake, and D. Gruber. 1993. Derivation of Sirt-Specific Ammonia Criteria for an Effluent-Dominated Headwater Stream. Environmental Toxicology and Chemistry, 12: 649-658.

Dillon, T.M., D.W. Moore, and A.S. Jarvis. 1994. The Effects of Storage Temperature and Time on Sediment Toxicity. Archives of Environmental Contamination and Toxicology, 27: 51-53.

Diplas, P. and J.B. Fripp. 1992. Properties of Various Sediment Sampling Procedures. Journal of Hydraulic Engineering, 118: 955-971.

Draves, J.F. and M.G. Fox. 1998. Effects of a Mine Tailings Spill on Feeding and Metal Concentrations in Yellow Perch. Environmental Toxicology and Chemistry, 17: 1626-1632.

Droppo, I.G. and C. Jaskot. 1995. Impact of River Transport Characteristics on Contaminant Sampling Error and Design. Environmental Science and Technology, 29: 161-170.

Dudka, S. and D.C. Adriano. 1997. Environmental Impacts of Metal Ore Mining and Processing: A Review. Journal of Environmental Quality, 26: 590-602.

Duursma, E.K. and M. Smies. 1982. Sediments and Transfer at and in the Bottom Interfacial Layer. *In:* Pollutant Transfer and Transport in the Sea. CRC Press. pp. 101-139.

Environment Canada. 1995. Guidance Document on Measurement of Toxicity Test Precision Using Control Sediments Spiked with a Reference Toxicant. Report EPS 1/RM/30.

Fent, K. and J. Hunn. 1995. Organotins In Freshwater Harbors And Rivers: Temporal Distribution, Annual Trends And Fate. Environ. Toxicol. Chem., 14: 1123-1132.

Flannagan, J.F. 1970. Efficiencies of Various Grabs and Corers in Sampling Freshwater Benthos. Journal Fisheries Research Board of Canada, 27: 1691-1700.

Ford, R.G., P.M. Bertsch, and K.J. Farley. 1997. Changes in Transition and Heavy Metal Partitioning during Hydrous Ion Oxide Aging. Environ. Sci. Technol., 31: 2028-2033.

Gagnier, D.L. and R.C. Bailey. 1994. Balancing Loss of Information and Gains in Efficiency in Characterizing Stream Sediment Samples. J. N. Am. Benthol. Soc., 13: 170-180.

Garner, F.C., M.A. Stapanian, and L.R. Williams. 1988. Composite Sampling for Environment Monitoring. pp. 363-374. Principals of Environ. Mon. American Chemical Soc., New York, NY.

Gilbert, R. and J. Glew. 1985. A Portable Percussion Coring Device for Lacustrine and Marine Sediments, Journal of Sediment Petrology, 55: 607-608.

Gilpin, B.R. and M.A. Brusven. 1976. Subsurface Sampler for Determining Vertical Distribution of Stream-Bed Benthos. The Progressive Fish-Culturist, 38: 192-194.

Glabbig, R.A. and S. Goldberg. 1988. Determination of Inorganic As (III) and As (III plus V) Using Automated Hydride-Generation Atomic-Absorption Spectrometry. Soil Sci. Soc. Am., 52: 536-537.

Grosheva, E.I. 1993. Mercury Transport, Transformation, and Bioaccumulation in the Ecosystem of Mercury-Stibium Geochemical Province. Water, Air, and Soil Pollution, 66: 381-388.

Hanes, E.C., J.J.H. Ciborowski, and L.D. Corkum. 1990. Standardized rearing materials and procedures for Hexagenia, a benthic bioassay organism: comparison of sediment types. Proc. 1990 Ontario Ministry of the Environ. Technol. Transfer Conf. on Environ. Res. Toronto, 1: 374-382.

Heimbach, F. 1985. Comparison of laboratory methods, using *Eisenia foetida* and *Lumbricus terrestris* for the assessment of the hazard of chemicals to earthworms. Z. Planzenkh. Pflanzensch., 92: 189-193.

Ho, K.T., L.J. Mills, C. Mueller, S.C. Anderson, and A.R. Malcolm. 1994. The Influence of Sediment Extract Fractionation Methods on Bioassay Results. Environmental Toxicology and Water Quality: An International Journal, 9: 145-154.

Janssen, R.P.T., W.J.G.M. Peijnenburg, L. Posthuma, and Marc A.G.T. Van Den Hoop. 1997. Equilibrium Partitioning of Heavy Metals in Dutch Field Soils. I. Relationship Between Metal Partition Coefficients and Soil Characteristics. Environ. Toxicol. Chem., 16: 2470-2478.

Janssen, R.P.T., L. Posthuma, R. Baerselman, H.A. Den Hollander, Rens P.M. Van Veen, and Willie J.G.M. Peijnenburg. 1997. Equilibrium Partitioning of Heavy Metals in Dutch Field Soils. II. Prediction of Metal Accumulation in Earthworms. Environ. Toxicol. Chem., 16: 2479-2488.

Jop, K.M. and A.M. Askew. 1994. Toxicity Identification Evaluation Using a Short-Term Chronic Test with *Ceriodaphnia dubia*. Bulletin Environ. Contam. Toxicol., 53: 91-97.

Kaddah, M.T. 1974. The Hydrometer Method for Detailed Particle-Size Analysis: 1. Graphical Interpretation of Hydromether Readings and Test of Method. Soil Science, 118: 102-107.

Kretzschmar, R. and H. Sticher. 1997. Transport of Humic-Coated Iron Oxide Colloids in a Sandy Soil: Influence of Ca2+ and Trace Metals. Environ. Sci. Technol., 31: 3497-3504.

Kriukov, P.A. and F.T. Manheim. 1982. Extraction and Investigative Techniques for Study of Interstitial Waters of Unconsolidated Sedimants: A Review. The Dynamic Environment of the Ocean Floor. Lexington Books. Washington D.C. pp. 3-26.

Krumgalz, B.S., G. Fainshtein, M. Sahler, and L. Gorfunkel. 1989. 'Field Error' Related to Marine Sediment Contamination Studies. Marine Pollution Bulletin, 20: 64-69.

Lanesky, D.E., B.W. Logan, R.G. Brown, and A.C. Hine. 1979. A New Approach to Portable Vibracoring Underwater and on Land. Journal of Sediment Petrology, 49: 654-657.

Lappalanien, K.M. 1982. Convection in Bottom Sediments and Its Role in Material Exchange Between Water and Sediments. Hydrobiologia, 86: 105-108.

Lee, S.-Z., H.E. Allen, C.P. Huang, D.L. Sparks, P.F. Sanders, and W.J.G.M. Peijnenburg. 1996. Predicting Soil-Water Partition Coefficients for Cadmium. Environmental Science and Technology, 30: 3418-3423.

Long, E.R., A. Robertson, D.A. Wolfe, J. Hameedi, and G.M. Sloane. 1996. Estimates of the Spatial Extent of Sediment Toxicity in Major U.S. Estuaries. Environmental Science and Technology, 30: 3585-3592.

Luoma, S.N. 1996. The Developing Framework of Marine Ecotoxicology: Pollutants as a Variable in Marine Ecosystem? Journal of Experimental Marine Biology and Ecology, 200: 29-55.

Luoma, S.N., C. Johns, N.S. Fisher, N.A. Steinberg, R.S. Oremland, and J.R. Reinfelder. 1992. Determination of Selenium Bioavailability to a Benthic Bivalve from Particulate and Solute Pathways. Environmental Science and Technology, 26: 485-491.

Luoma, S.N. and D.J.H. Phillips. 1988. Distribution, Variability, and Impacts of Trace Elements in San Francisco Bay. Marine Pollution Bulletin, 19: 413-425.

Lyons, W.B., H.E. Gaudette, and G.M. Smith. 1979. Pore water Sampling in Anoxic Carbonate Sediments: Oxidation Artefacts. Nature, 277: 48-49.

Lyons, W.B., R.M. Lent, W.C. Burnett, P. Chin, W.M. Landing, W.H. Orem, and J.M. McArthur. 1996. Jellyfish Lake, Palau: Regeneration of C, N, Si, and P in anoxic marine lake sediments. Limnology and Oceanography, 41: 1394-1403.

Malley, D.F. and P.C. Williams. 1997. Use of Near-Infrared Reflectance Spectroscopy in Prediction of Heavy Metals in Freshwater Sediment by Their Association with Organic Matter. Environmental Science and Technology, 31: 3461-3467.

Manning, B.A. and D.A. Martens. 1997. Speciation of As(III) and As(V) in Sediment Extracts by High-Performance Liquid Chromatography – Hydride Generation Atomic Absorption Spectrophotometry. Environmental Science and Technology, 31: 171-177.

McCloskey, J.T., I.R. Schultz, and M.C. Newman. 1998. Estimating the Oral Bioavailability of Methylmercury to Channel Catfish. Environmental Toxicology and Chemistry, 17: 1524-1529.

Maruya, K.A., R.W. Risebrough, and A.J. Horne. 1996. Partitioning of polynuclear aromatic hydrocarbons between sediments from San Franscisco Bay and their pore waters. Environ. Sci. Technol., 30: 2942-2947.

Miller, G.C., W.B. Lyons, and A. Davis. 1996. Understanding the Water Quality of Pit Lakes. Environmental Science and Technology, 30: 118-123.

Montgomery, J.R., M.T. Price, J. Holt, and C. Zimmermann. 1981. A Close-Interval Sampler for Collection of Sediment Pore Waters for Nutrient Analyses. Estuaries, 4: 75-77.

Moody, J.R. and R.M. Lindstrom. 1977. Selection and Cleaning of Plastic Containers for Storage of Trace Element Samples. Analytical Chem., 49: 2264-2267

Morillo, E., T. Undabeytia, and C. Maqueda. 1997. Adsorption of Glyphosate on the Clay Mineral Montmorillonite: Effect of Cu(II) in Solution and Adsorbed on the Mineral. Environmental Science and Technology, 31: 3588-3592.

Nath, B., V. Nagender, S. Rajaraman, and A.V. Mudholkar. 1988. Indian Journal of Marine Sciences, 17: 71-72.

Naylor, C. and C. Rodrigues. 1995. Development of a test method for *Chironomus riparius* using a formulated sediment. Chemosphere, 31: 3291-3303.

Neuhauser, E.F., R.C. Loehr, and M.R. Malecki.1986. Contact and artificial soil tests using earthworms to evaluate the impact of wastes in soil. *In*: J.K. Petros, Jr., W.J. Lacey, and R.A. Conway (eds.) Hazardous and Industrial Solid Waste Testing: Fourth Symposium. Amer. Soc. Testing and Materials, Philadelphia, PA. pp. 192-203.

Neumann, H.H. and W. Ahlf. 1995. Fate of copper and cadmium in a sediment-water system, and effect on chitin degrading bacteria. Acta Hydrochimica et Hydrobiologica, 23: 72-75.

O'Day, P.A., S.A. Carroll, and G.A. Waychunas. 1998. Rock-Water Interactions Controllong Zn, Cd, and Pb Concentrations in Surface Waters and Sediments, U.S. Tri-State Mining District 1. Molecular Identification Using X-ray Absorption Spectroscopy. Environmental Science and Technology, 32: 943-955.

Othoudt, R.A., J.P. Giesy, K.R. Grzyb, D.A. Verbrugge, R.A. Hoke, J.B. Drake, and D. Anderson. 1991. Evaluation of the Effects of Storage Time on the Toxicity of Sediments. Chemosphere, 22: 801-807.

Palmer, F.B., C.A. Butler, M.H. Timperley, and C.W. Evans. 1998. Toxicity to Embryo and Adult Zebrafish of Copper Complexes with Two Malonic Acids as Models for Dissolved Organic Matter. Environmental Toxicology and Chemistry, 17: 1538-1545.

Pantani, C., N. Spreti, M.C. Maggitti, and R. Germani. 1995. Acute Toxicity of Some Synthetic Cationic and Zwitterionic Surfactants to Freshwater Amphipod *Echinogammarus tibaldii*. Bulletin of Environmental Contamination and Toxicology, 55: 179-186.

Pascoe, D., A.F. Brown, B.M.J. Evans, and C. McKavanagh. 1990. Effects and fate of Cd during toxicity tests with *Chlronomus riparius* – the influence of food and artificial sediment. Arch. Environ. Contam. Toxicol., 19: 872-877.

Pathirana, S., D.W. Connell, and P.D. Vowles. 1994. Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Roadway System. Ecotoxicology and Environmental Safety, 28: 256-269.

Rendell, P.S., G.E. Batley, and A.J. Cameron. 1980. Absorption as a Control of Metal Concentrations on Sediment Extracts. Environmental Science and Technology, 14: 314-318.

Rowan, D.J. and J. Kalff. 1993. Predicting Sediment Metal Concentrations In Lakes Without Point Sources. Water, Air, and Soil Pollution, 66: 145-161.

Rutherford, D.W., C.T. Chiou, and D.E. Kile. 1992. Influence of soil organic matter composition on the partition of organic compounds. Environ. Sci. Technol., 26: 336-340.

Sauve, S., A. Dumestre, M. McBride, and W. Hendershot. 1998. Derivation of Soil Quality Criteria Using Predicted Chemical Speciation of Pb2+ and Cu2+. Environmental Toxicology and Chemistry, 17: 1481-1489.

Sijm, R.T.H.M., M. Haller, and S.M. Schrap. 1997. Influence of Storage an Sediment Characteristics and of Drying Sediment on Sorption Coefficients of Organic Contaminants. Bulletin of Environmental Contamination and Toxicology, 58: 961-968.

Silver, M.L. 1972. Handling and Storage of Chemically and Biologically Active Ocean Sedimants. MTS Journal, 6: 32-36.

Singer, J.K., J.B. Anderson, M.T. Ledbetter, I.N. McCave, K.P.N. Jones, and R. Wright. 1988. Journal of Sedimentary Petrology, 58: 534-543.

Skaare, J.U., E. Degre, P.E. Aspholm, and K.I. Ugland. 1994. Mercury and Selenium in Arctic and Coastal Seals Off the Coast of Norway. Environmental Pollution, 85: 153-160.

Sohrin, Y., M. Matsui, M. Kawashima, M. Hojo, and H. Hasegawa. 1997. As Biogeochemistry Affected by Eutrophication in Lake Biwa, Japan. Environ. Sci. Technol., 31: 2712-2720.

Stackhouse, R.A. and W.H. Benson. 1989. Interactions of Humic Acids and Selected True Metals: Influence on Bioaccumulation in Daphnids. Environ. Toxicol. Chem., 8: 639-644.

Suedel, B.C., R.S. Hartzell, C.W. Williams, and R.A. Connelly. 1994. Development of a standardized sediment reference toxicant test using formulated sediment and copper sulfate. Abstr. HC04, p. 223. Annu. Meet. Soc. Environ. Toxicol. Chem., Denver, CO.

Suedel, B.C., and J.H. Rodgers, Jr. 1994. Development of formulated reference sediments for freshwater and estuarine sediment testing. Environ. Toxicol. Chem., 13: 1163-1175.

Suedel, B.C., E. Deaver, and J.H. Rodgers, Jr. 1996. Experiment factors that may affect toxicity of aqueous and sediment-bound copper to freshwater organisms. Arch. Environ. Contam. Toxicol., 30: 40-46.

Suedel, B.C., E. Deaver, and J.H. Rodgers, Jr. 1996. Formulated sediment as a reference and dilution sediment in definitive toxicity tests. Arch. Environ. Contam. Toxicol., 30: 47-52.

Suedel, B.C. and J.H. Rodgers, Jr. 1996. Toxicity of fluoranthene to *Daphnia magna, Hyalella azteca, Chironomus tentans*, and *Stylaria lacustris* in water-only and whole sediment exposures. Bull. Environ. Contam. Toxicol., 57: 132-138.

Swift, D.J.P., J.R. Schubel, and R.W. Sheldon. 1972. Size Analysis of Fine-Grained Suspended Sediments: A Review. Journal of Sedimantary Petrology, 42: 122-134.

Tatem, H.E., 1990. Bioaccumulation of Polychlorinated Biphenyls and Metals from Contaminated Sediment by Freshwater Prawns, *Macrobracium rosenbergii*, and Clams, *Corbicula fluminea*, Archives of Environmental Contamination & Toxicology, 15: 171-183.

Tessier, A., P.G.C. Campbell, and M. Bisson. 1980. Trace Metal Speciation in the Yamaska and St. Francois Rivers (Quebec). Canadian Journal of Earth Science, 17: 90-105.

Tessier, A., P.G.C. Campbell, and M. Bisson. 1982. Particulate Trace Metal Speciation in Stream Sediments and Relationships with Grain Size: Implications for Geochemical Exploration. Journal of Geochemical Exploration, 16: 77-104.

Thoms, S.R., G. Matisoff, P.L. McCall, and X. Wang. 1995. Models for Alteration of Sedimants by Benthic Organisms. Water Environment Research Foundation.

Thomson, E.A., S.N. Luoma, D.J. Cain, and C. Johansson. 1980. The Effect of Sample Storage on the Extraction of Cu, Zn, Fe, Mn, and Organic Material from Oxidized Estuarine Sediments. Water Air and Soil Pollution, 14: 215-233.

Titus, J.A. and R.M. Pfister. 1982. Effects of pH, temperature, and Eh on the uptake of calcium by bacteria and an artificial sediment. Bull. Environ. Contam. Toxicol., 28: 697-704.

Tokunaga, T.K., S.R. Sutton, S. Bait, P. Nuessle, and G. Shea-McCarthy. 1998. Se Diffusion and Reduction at the Water-Sediment Boundry: Micro-XANES Spectroscopy of Reactive Transport. Environmental Science and Technology, 32: 1092-1098.

Van Dam, L. 1995. The Preparation and Use of Gels for Measuring Pollutants and Natural Species in the Aquatic Environment. 1995 Overseas Travel Report Visit to Lancaster University, UK. Internal Report.

van den Burg, G.A., J.P. Gustav Loch, Lambertus M. van der Heijdt, and J.J.G. Zwolsman. 1998. Vertical Distribution of Acid-Volatile Sulfide and Simultaneously Extracted Metals in a Recent Sedimentation Area of the River Meuse in the Netherlands. Environmental Toxicology and Chemistry, 17: 758-763.

Veltz, I., F. Arsac, S. Biagianti-Risbourg, F. Habets, H, Lechenault, and G. Vernet. 1996. Effects of Platinum (Pt^{4+}) on *Lumbriculus variegatus* Müller (Annelida, Oligochaetae): Acute Toxicity and Bioaccumulation. Archives Environ. Contam. Toxicol., 31: 63-67.

Walsh, G.E., D.E. Weber, L.K. Brashers, and T.L Simon. 1990. Artificial sediment for use in tests with wetland plants. Environ. Exper. Botany, 30: 391-396.

Walsh, G.E., D.E. Weber, T.L. Simon, L.K. Brashers, and J.C. Moore. 1991a. Use of marsh plants for toxicity testing of water and sediment. *In:* J.W. Gorsuch, W.R. Lower, W. Wang, and M.A. Lewis (eds.) Plants for Toxicity Assessment: Second Volumne, ASTM STP 1115. Amer. Soc. Testing. and Materials, Philadelphia. pp. 341-354.

Walsh, G.E., D.E. Weber, T.L. Simon, and L.K. Brashers. 1991b. Toxicity tests of effluents with marsh plants in water and sediment. Environ. Toxicol. Chem., 10: 517-525.

Walsh, G.E., D.E. Weber, L.K. Esry, M.T. Nguyen, J. Noles, and B. Albrecht. 1992. Synthetic substrata for propagation and testing of soil and sediment organisms. Pedobiologia, 36: 1-10.

Walsh, G.E., D.E. Weber, M.T. Nguyen, and L.K. Esry. 1991c. Responses of wetland plants to effluents in water and sediment. Environ. Exper. Botany, 31: 351-358.

Warren, L.A., P.M. Outridge, and A.P. Zimmerman. 1995. Geochemical partitioning and bioavailability of Cu to aquatic plants in an artificial oxide-organic sediment. Hydrobiologia, 304: 197-207.

Watzin, M.C. and P.F. Roscigno. 1994. Response of estuarine benthic communities to zinc contamination: tests using formulated sediments. Abstr. HC08, p. 224. Annu. Meet. Soc. Environ. Toxicol. Chem., Denver, CO.

Watzin, M.C., P.F. Roscigno, and W.D. Burke. 1994. Community-level field method for testing the toxicity of contaminated sediments in estuaries. Environ. Toxicol. Chem., 13: 1187-1193.

Webster, I.T., G.J. Hancock, and A.S. Murray. 1994. Use of Radium Isotopes to Examine Pore-water Exchange in an Estuary. Limnology and Oceanography, 39: 1917-1927.

Wen, X., Q. Du, and H. Tang. 1998. Surface Complexation Model for the Heavy Metal Adsorption on Natural Sediment. Environmental Science and Technology, 32: 870-875.

Wenholz, M. and R. Crunkilton. 1995. Use of Toxicity Identification Evaluation Procedures In the Assessment of Sediment Pore Water Toxicity from an Urban Stormwater Retention Pond in Madison, Wisconsin. Bulletin of Environmental Contamination and Toxicology, 54: 676-682.

West, C.W., G.L. Phipps, R.A. Hoke, T.A. Goldenstein, F.M. VanderMeiden, P.A. Kosian, and G.T. Ankley. 1994. Sediment Core versus Grab Samples: Evaluation of Contamination and Toxicity at a DDT-Contaminated Site. Ecotoxicology and Environmental Safety, 28: 208-220.

Whiticar, M.J. 1982. Determination of Interstitial Gases and Fluids in Sediment Collected with an in situ Sampler. Anal. Chem., 54: 1796-1798.

Winter, S. 1996. Cd Uptake Kinetics By Freshwater Mollusc Soft Body Under Hard And Soft Water Conditions. Chemosphere, 32: 1937-1948.

Yee, S., M. Van Rikxoort, and D. McLeay. 1992. The effect of holding time on *Eohaustorius washingtonianus* during ten-day sediment bioassays and reference toxicant tests. Report prepared for Environment Canada and the Inter-Governmental Aquatic Toxicity Group, North Vancouver, BC 53 pp.

Yin, Y., H.E. Allen, C.P. Huang, D. Sparks, and P.F. Sanders. 1997. Kinetics of Mercury(II) Adsorption and Desorption on Soil. Environmental Science and Technology, 31: 496-503.